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OPTIMIZATION OF GC/MS BASED TENAX COLLECTION METHOD FOR TOXIC ORGANICS

by

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The sampling of vapor-phase organics in the presence of reactive inorganics using the Tenax GC sampling cartridge was investigated. To differentiate between pollutants in air and those formed from in situ artifact reactions, deuterated organics were employed in both laboratory and field experiments; and any subsequent artifact products were detected by capillary gas chromatography/mass spectrometry/computer [$(GC)^2$/MS/COMP] techniques. Artifacts produced by Tenax GC itself and by reactions between adsorbed species were investigated using statistical methods.

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ABSTRACT

The sampling of vapor-phase organics in the presence of reactive inorganics using the Tenax GC sampling cartridge was investigated. To differentiate between pollutants in air and those formed from *in situ* artifact reactions, deuterated organics were employed in both laboratory and field experiments; and any subsequent artifact products were detected by capillary gas chromatography/mass spectrometry/computer [HRGC/MS/COMP] techniques. Artifacts produced by Tenax GC itself and by reactions between adsorbed species were investigated using statistical methods.

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SECTION 1

INTRODUCTION

The characterization and measurement of extremely minute amounts of hazardous compounds in ambient air has for many years been seriously hampered by the lack of reliable sampling systems. Techniques have been developed to concentrate organic vapors from large volumes of atmosphere and to transfer the collected vapors to an analytical system.[1-5]

There is, however, a paucity of experimental data concerning artifact studies on collection devices for vapor-phase organics. There has been a propensity for investigators to prematurely accept the viability of the collection step while emphasizing other steps in development of analytical procedures. In fact, the literature is replete with analytical methods for analysis of a few vapor-phase components in complex mixtures using a variety of instrumental methods.[5] Nonetheless, it should be noted that none of these procedures can be distinguished as superior to others since the collection method is a common denominator among all the analytical methods and appears to be the weakest link.

With the elucidation of nitrosamines in ambient air, serious consideration was given to potential artifact formation during collection.[1-4] In fact, a metamorphosis of collection methods for nitrosamines occurred. Artifacts associated with cryogenic traps were readily apparent, and modifications ensued which eventually led to the use of a sorbent cartridge impregnated with sulfamic acid to inhibit the <u>in situ</u> nitrosation of secondary amines.[5]

An approach to the detection, identification and quantification of halogenated hydrocarbons in the ambient air has employed the use of a Tenax GC cartridge in combination with high resolution gas chromatography/mass spectrometry/computer [HRGC/MS/COMP] analysis. Our primary concern was with the use of the Tenax GC sorbent which has been previously employed for

collecting vapor-phase organics in ambient air. Since the Tenax GC cartridge may concentrate reactive compounds from an atmosphere containing, for example, ozone, NO_x, molecular halogen (Cl_2, Br_2); in situ formation of artifact products may occur, even though inorganic gases do not appreciably accumulate on the sorbent. Preliminary studies have been conducted which indicated that a more in-depth study was needed.[1-5]

The objectives of this research program were: (a) to examine the potential troublesome chemical group types which exhibit reactivity with the commonly occurring inorganic gases in ambient air; (b) to conduct a series of controlled laboratory experiments to determine the extent, if any, of artifact problems associated with the direct interaction of these inorganic gases with Tenax GC itself; (c) to evaluate the artifact problems, if any, associated with organics on Tenax GC in the presence of atmospheric concentrations of inorganic gases; (d) to develop a means of minimizing potential artifacts if they exist; and (e) to evaluate and apply corrective measures which minimize artifact production under field sampling conditions.

SECTION 2

CONCLUSIONS

ARTIFACTS PRODUCED FROM TENAX GC ITSELF

(1) The main artifacts produced from Tenax GC were: benzaldehyde, acetophenone, phenol, α-hydroxyacetophenone, acetic acid and ethylene oxide;

(2) The main factors determining the quantities of artifacts generated were (in order of decreasing importance):
   (a) ozone concentration of sampled air;
   (b) age of the Tenax cartridge;
   (c) humidity of the sampled air;
   (d) concentration of nitric oxides; and
   (e) concentrations of other reactive compounds (sulfur oxides, chlorine).

ARTIFACT REACTIONS OF ADSORBED SPECIES

Artifact reactions of adsorbed species were:

(1) Relatively unimportant for aromatics and saturated halogenated compounds and

(2) Significant for more reactive compounds: e.g., unsaturated compounds such as trichloroethylene, and tetrachloroethylene.

SODIUM THIOSULFATE IMPREGNATED FILTERS

Sodium thiosulfate impregnated filters were:

(1) Effective in reducing artifacts generated by Tenax GC itself and

(2) Effective in reducing artifact reactions of reactive adsorbed species.

Use of sodium thiosulfate impregnated glass fiber filters for sampling with Tenax GC cartridges is strongly recommended.

SECTION 3

RECOMMENDATIONS CONCERNING CORRECT PROCEDURES FOR COLLECTING VOLATILE ORGANICS IN AIR WITH TENAX GC CARTRIDGES

Based on the results of laboratory and field experiments on artifact formation, three important recommendations are made:

1. Sodium thiosulfate impregnated glass fiber filters should be used, with an expected improvement in:
   (a) collection efficiency of compounds reactive toward ozone (e.g.,unsaturated compounds) and
   (b) Tenax GC sorbent stability which will result in fewer artifact products.
2. The selection of the sampling volume must consider humidity in the air (80 to 100%) thereby avoiding excessive artifact formation, and at the same time, early breakthrough for the more volatile components sampled.
3. If the quantities found for benzaldehyde, acetophenone, and phenol are more than 1,000 ng/cartridge, quantitation for these compounds can be conducted.

SECTION 4

LABORATORY EXPERIMENTS ON ARTIFACT REACTIONS IN AIR SAMPLING FOR VOLATILE ORGANICS

ARTIFACTS PRODUCED FROM TENAX GC ITSELF

Experimental Procedures

Tenax GC Cartridges--

The Tenax GC sorbent was prepurified by the following sequence of operations:

(1) Methanol extraction (distilled in glass, redistilled methanol) for 24 h in a Soxhlet apparatus;

(2) Pentane extraction (distilled in glass, redistilled pentane) for 24 h in a Soxhlet apparatus;

(3) Drying at room temperature under nitrogen flow for 24 h; and

(4) Drying in vacuum overnight at approximately 100°C.

Clean glass cartridges of 100 mm length and 13 mm ID were filled with sorbent; the 60 mm sorbent bed held in place by glass wool plugs.

The final purification step was thermal conditioning under helium flow (~30 mL/min) at 250-270°C for a minimum of 2.5 h.

The weight of Tenax GC sorbent in cartridges was:

mean = 1.113 g;
standard deviation = 0.093 g;
for n = 12 cartridges.

Experimental Set-up For Artifact Formation Studies--

A schematic of the experimental set-up is presented in Figure 1. The list of reactive species in sampled air which could potentially generate artifacts is presented in Table 1. The clean air source was a Matheson Ultra-Zero air supply. The hydrocarbon content in air was less than 0.1 ppm as CH_4. As a supplementary modification a Teflon membrane filter and a drierite/molecular sieve cartridge were installed after the pressure regulator.

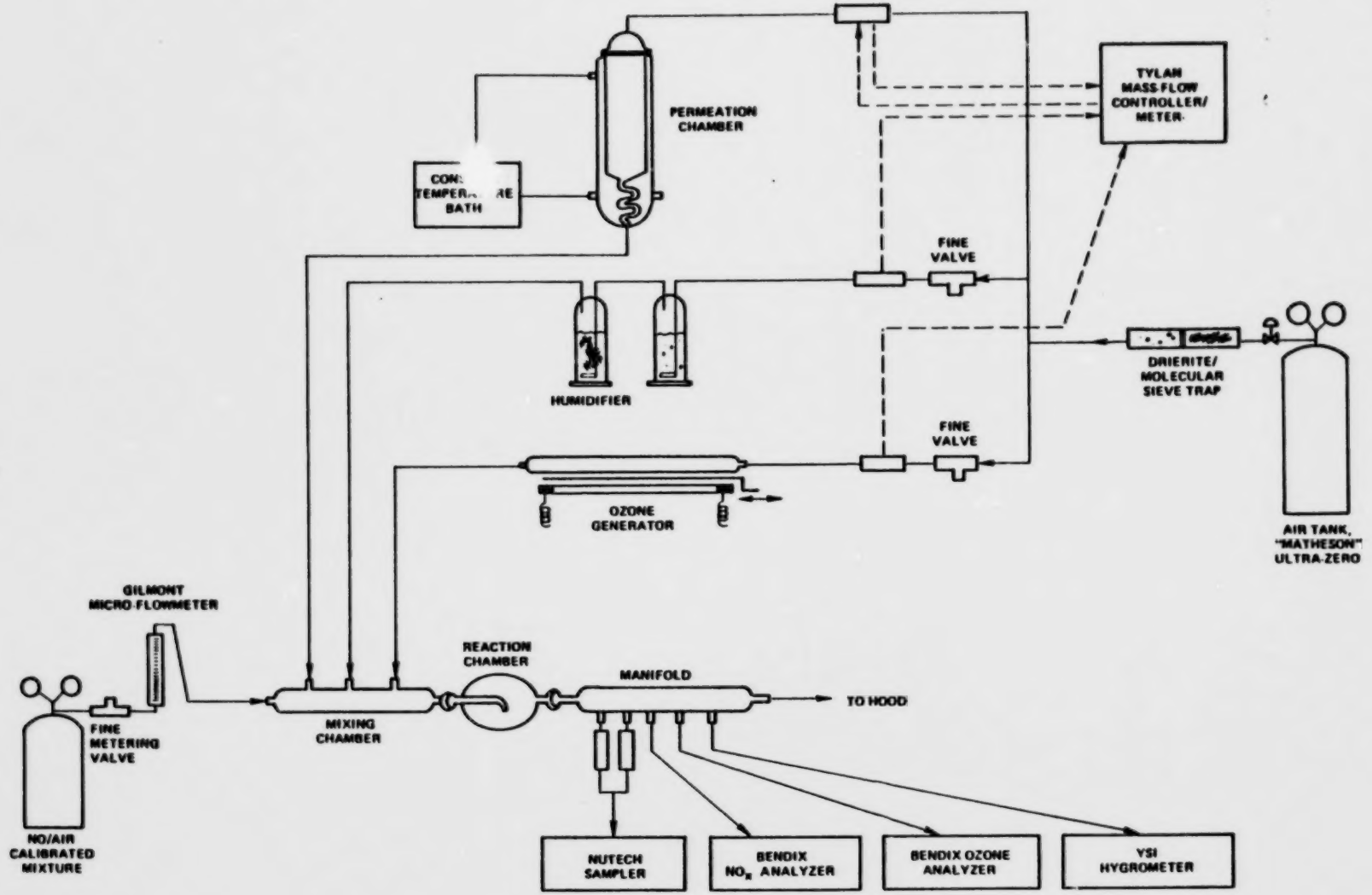


Figure 1. Experimental set-up for artifacts on Tenax GC cartridges studies. (All lines leading to or from devices were made of Teflon ®).

Table 1. REACTIVE INORGANIC SPECIES IN SAMPLED AIR

Substance	Concentration Range	Source	Monitoring Method
Ozone, O_3	0 - 200 ppb	UV (254 nm) irradiation	Bendix Ozone Monitor (Chemiluminescence)
Nitric Oxides; NO, NO_2	0 - 300 ppb	NO/air calibrated mixture	Bendix $NO/NO_2/NO_x$ Monitor (Chemiluminescence)
Sulfur Oxides; SO_2, SO_3	0 - 300 ppb	SO_2/air calibrated mixture	Gas phase titration, Bendix Ozone Monitor
Chlorine, Cl_2	0 - 175 ppb	Permeation devices (VICI Metronics) wafer types	Gravimetric check of permeation rates
Water, H_2O	0 - 100% relative humidity	Bubbling/mixing	Yellow Springs Inst. Hydrometer

Three Teflon® lines from the clean air source led to:

(1) the permeation chamber;

(2) the humidifier line;

(3) the ozone generator.

The permeation chamber was thermostated with water circulation in the external mantle. With permeation devices for chlorine in the permeation chamber, the total flow in the system and the permeation rate allowed a known chlorine concentration in the outflowing air to be set.

The humidifier line consisted of two 500 mL gas washing bottles. The first bottle was filled with distilled water and the second with just 3 mm glass rings. The air passing through the first washing bottle reached practically 100% humidity (at the corresponding temperature); aerosols from the air stream were separated in the second washing bottle. Measurements with a YSI hygrometer confirmed that the humidity of air leaving the humidifier line was essentially at 100%. By means of the ratio of flows through the humidifier line and the other lines, the final humidity of the air mixture was easily controlled.

Ozone was generated using a fused quartz tube irradiated by a UV lamp. A sliding cover on the UV lamp was adjustable to different positions (mm graduations) and that parameter and the value of the air flow through the quartz tube determined the ozone concentration in the gas mixture. An approximate calibration curve is presented in Figure 2; however, the graph was utilized only for assisting in setting the parameters of an experiment. The actual ozone concentration was always monitored by the Bendix ozone analyzer.

Since the ozone output of the ozone generator was very stable, it was used for checking the readings of the Bendix ozone analyzer from time to time. The values from Table 2 were determined with a Dasibi ultraviolet photometer (*vide infra*).

The air passing through the a, b, and c lines was regulated by:

(a) Tylan mass-flow controller;

(b) and (c) Nupro fine metering valves (3° stem) and monitored by Tylan mass flow meters.

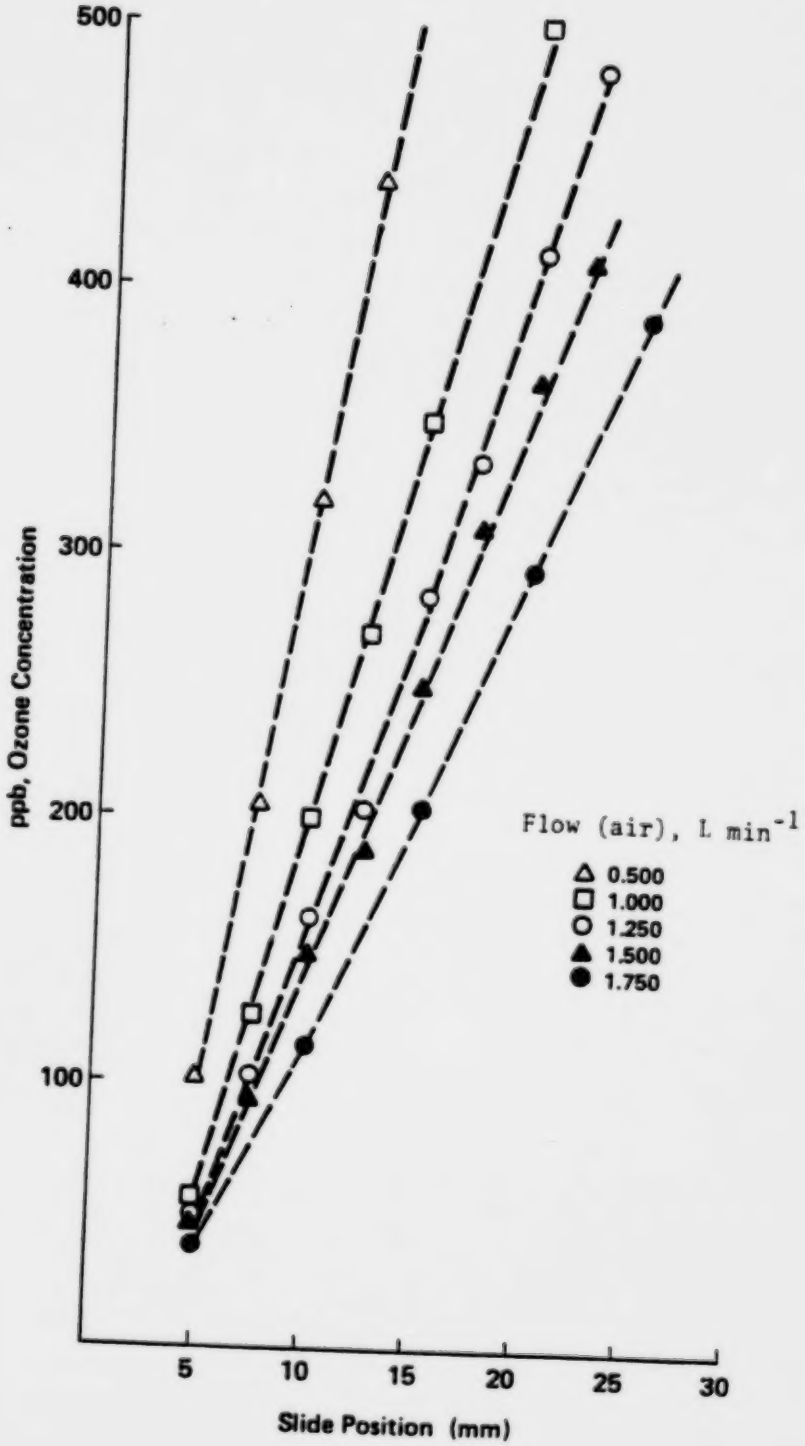


Figure 2. Ozone generator calibration.

Table 2. BENDIX OZONE ANALYZER CALIBRATION

Analyzer Bendix 8002, S/N 100586
Settings: Initial - Zero: 015, Span: 554
Final - Zero: 015, Span 570
Range: 0-0.5 ppm
Time Constant: 10 sec
Sample and Ethylene Flow = 350 mL/min
Calibration Photometer: Dasibi, Model 1003AH, S/N 2342
Clean Air Flow: 2.490 L/min

Ozone Generator Sleeve Setting, mm	Photometer Ozone[a] ppm	Bendix Ozone Concentration, ppm	Difference[a,b] ppm	Percent Difference
Precalibration Check:				
8.0	0.529	0.485	-0.088	-8.3
After Span Adjustment:				
Closed	0.000	0.000	0.000	-
60	0.390	0.390	0.000	0.0
50	0.313	0.310	-0.003	-0.3
40	0.287	0.245	-0.002	-0.8
30	0.176	0.172	-0.004	-2.3
20	0.105	0.105	0.000	0.0
10	0.036	0.040	+0.004	+11.1

[a]As read from digital display at Dasibi photometer, less than zero offset.

[b]As read from front panel meter of Bendix analyzer.

The Tylan mass flow controller/meter was calibrated against a soap bubble-meter (2 L volume), and readings were converted to real flows using calibration charts. The calibration charts, with a satisfactory precision, can be substituted by straight line approximations although the patterns of signs for the differences between calculated and measured values clearly indicate a curvature of the plots.

The concentration of nitric oxides in the final mixture was controlled by the (small) flow coming from a cylinder with a calibrated mixture (NO/air), regulated by a fine metering valve (Nupro, 1° tapered stem) and monitored with a calibrated differential pressure flowmeter or a high precision Gilmont Microflow meter type F-3060 A (0.02 - 15 mL/min range for air). Alternatively, an SO_2/air calibrated mixture can be used to generate a known concentration of SO_x in the final mixture.

All flows were mixed together in the mixing chamber and, after passing through a reaction chamber, were directed to the sampling manifold. Nitric oxides, sulfur oxides, and ozone concentrations, and percent humidity of the mixture were monitored.

The Bendix Nitric Oxides Monitor was calibrated with a mixture prepared from clean air (line a, with mass-flow controller) and an NO/air calibration mixture (approximately 49.8 ppm NO, <0.1 ppm NO_2, AirCo) for the NO mode and NO_x mode. With the ozone generator at a high setting, and the prepared mixture flowing through the generator, NO was quantitatively converted to NO_2, and the Bendix monitor was calibrated in the NO_2 mode.

The Bendix Ozone Monitor was calibrated against a Dasibi Ultraviolet Photometer.[6,7] The schematic of the configuration used in calibrating the ozone monitor is presented in Figure 3. The calibration results are presented in Table 2.

The total sulfur oxides concentration was known from flow rates and the SO_2/air calibrated mixture concentrations. The percent conversion of SO_2 to SO_3 via reaction with ozone was calculated by gas-phase titration using the ozone monitor readings, with and without SO_2 added to the total flow.

The Yellow Spring Instrument Model 91 Dew Point Hygrometer was equipped with a humidity sensor consisting of a bobbin assembly and a spool wound

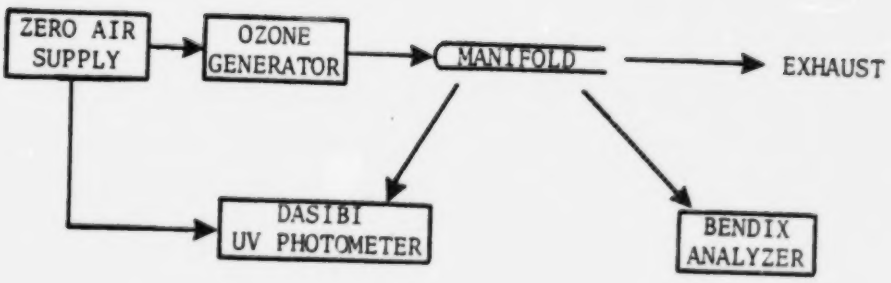


Figure 3. Schematic of configuration used in calibrating the ozone monitor.

Table 3. GAS CHROMATOGRAPHIC ANALYSIS OF TENAX GC CARTRIDGES

Instrument:	Varian 3700, FID Detector, CDS-111C data system
Column:	50 m fused silica, wide bore capillary column, Carbowax 20M stationary phase (Hewlett-Packard)
Thermal Desorption:	carrier gas - helium, 10 mL/min; desorption temperature: 270°C; cryogenic trap temperature - low, -196°C (liquid N_2), high + 250°C; desorption time - 8 min; heating time, trap - 4 min
Carrier Gas, Helium:	approximately 1 mL/min
Temperature Program:	70°C/10 min; 70 to 190°C/4°C/min; 190°C/10 min
Detector:	30 mL/min H_2; 250 mL/min air
Integrator:	CDS 111C, peak width parameter 4; signal/noise parameter 4

with lithium chloride impregnated wicking. The electrical conductivity of the sensor was humidity dependent. The front panel meter of the instrument directly reads Dew Point Temperature (range - 12°C to 42°C) and also corresponding water vapor pressures (2 to 60 mm Hg).

A Nutech sampling pump sampled air through a pair of Tenax GC cartridges in a parallel configuration with a flow rate of 1 liter/min.

High Resolution Gas Chromatographic Analysis of Tenax GC Cartridges--

For the qualitative and quantitative analysis of Tenax GC degradation products, the thermal desorption/high resolution GC method was used. The analysis parameters are listed in Table 3.

Gas Chromatography/Mass Spectrometry Analysis of Tenax GC Cartridges--

The GC/MS analysis parameters are listed in Table 4.

Tenax GC Cartridges Loaded with Standards--

A "flash-evaporation" system was used for loading standards onto Tenax GC cartridges and is shown in Figure 4.

Helium at a flowrate of approximately 75 mL/min was purified by activated charcoal filtration and cryogenic cooling (liquid nitrogen). A 125 mL glass bulb with a silicone rubber septum injection port and two Teflon stopcocks was heated to 100-110°C with a Briskheat® heating tape.

Standards in methanol were gravimetrically determined by a Mettler microbalance (0.000001 g precision) and injected (using a Hamilton microsyringe) into the glass bulb. The helium flow swept the vapors through the Tenax GC cartridge. The helium flow through the cartridge proceeded for 10 min.

Assuming complete mixing in the glass bulb, the concentration of injected compounds in the outflowing helium after 10 min will be (the vaporization can be considered instantaneous):

$$C = C_o \exp(-Fxt/V) = C_o \exp(-75 \times 10/125) = 0.00248 \cdot C_o$$

where:

C = final concentration

C_o = initial concentration

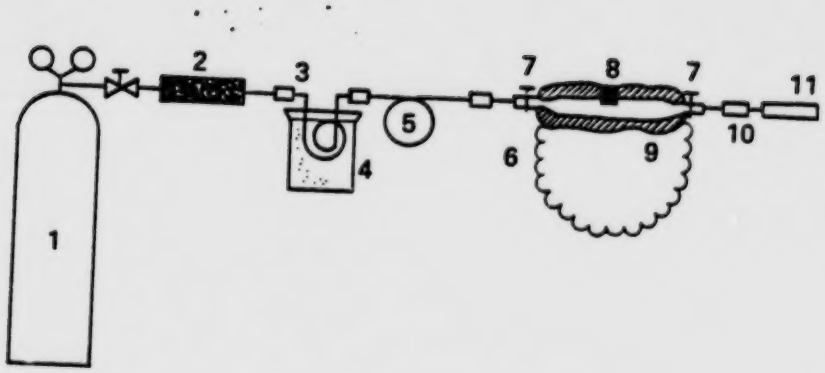
F = flow rate (mL/min)

V = volume, L.

or less than 0.25% of the initial concentration.

Table 4. GAS CHROMATOGRAPHY/MASS SPECTROMETRY ANALYSIS OF TENAX GC CARTRIDGES

Instrument:	Finnigan 3300
Gas Chromatography:	Thermal desorption - time, 8 min; - helium flow, 15 mL/min Columns: (a) Carbowax 20M fused silica, wide bore, 50 m Temperature program: 70°C, 10 min 70 to 190°C, 4°C/min (b) OV-101 fused silica, 60 m Temperature program: 40°C, 5 min 40 to 250°C, 2°C/min Flow rate, He carrier gas, 2.6 mL/min
Mass Spectrometry:	1.9 sec/scan m/z range: 35 to 300 Library search: INCOS software



Legend:

1. Helium tank
2. Activated charcoal trap
3. Cryogenic trap
4. Dewar flask with liquid nitrogen
5. 1 ft Ni tubing, ¼ in. O D
6. Glass bulb, 125 mL
7. Teflon stopcocks
8. Injection port with silicone rubber septum
9. Heating tape
10. Teflon union
11. Tenax cartridge

Figure 4. Experimental setup for loading Tenax GC cartridges with standards.

Alternatively, when permeation tubes were available, the system in Figure 1 was used for loading cartridges with very low concentrations of known quantitites of standards. To avoid adsorption errors, the system was equilibrated overnight with permeation tubes in the permeation chamber.

Ozone-Nitric Oxides - Humidity Effects

A factorial experiment 2^3 was planned,[8] in order to assess the ozone/nitric oxides/humidity combination effects. For quantitative analysis, the gas chromatographic system was calibrated with external standards. The identity of the major Tenax GC decomposition products was established by GC/MS methods.

Clean, "virgin" Tenax GC cartridges were exposed to air containing $O_3/NO_x/H_2O$; the pertinent information regarding Tenax GC cartridge exposure is listed in Table 5.

Gas Chromatography-Mass Spectrometry Analysis of Exposed Tenax GC Cartridges--

The peaks detected by total ion current monitoring with their retention times are listed in Table 6. The identity of major peaks was established by a INCOS software library search and confirmed by comparison with literature data[9]. The relevant mass spectral data are presented in Table 7. The presence of ethylene oxide and acetic acid as Tenax GC decomposition products suggests a ketene-type decomposition process of the poly(phenylene-oxide) polymer.

The early eluting peaks (on both columns), as confirmed by mass fragmentograms (m/z = 57.00 $\pm$ 0.5 a.m.u.), are hydrocarbons which can probably be traced to the purification step (specifically the pentane extraction).

The most important Tenax GC decomposition products were benzaldehyde, acetophenone, and phenol. The chemical structure of these products indicates ozonolysis as the major chemical reaction of the polymer or impurities embedded in it. After the breakdown of the polymer backbone, further reactions of the primary degradation products lead to the relatively stable compounds actually detected. This result is in agreement with many reports that the main degradative mechanism of polymeric materials is an interaction with atmospheric ozone[10].

Table 5. OZONE - NITRIC OXIDES - HUMIDITY EXPOSURE OF TENAX GC CARTRIDGES

Cartridge	Tenax GC, grams	Air Sampled		Ozone Conc., ppb	Nitric Oxides		Conc., NO_x ppb	Water Vapor mm Hg	Analysis
		Vol., L	Time, Min		NO ppb	NO_2 ppb			
1	2	3	4	5	6	7	8	9	10
A1	1.152	0	0	0	0	0	0	0	GC
A2	0.970	30	30	90	30	120	150	9.7	GC
A3	1.140								
A4	1.206	30	30	200	0	150	150	9.7	GC
A5	1.068								
A6	1.103	0	0	0	0	0	0	0	GC
A7	1.031	30	30	150	0	150	150	16.5	GC
A8	1.200								
A9	1.170	30	30	90	30	130	160	16.5	GC
A10	1.243								
A11	0.951	30	30	0	0	0	0	0	GC
A12	1.116								
B1	0.862	30	29	102	86	240	326	7.8	GC
B2	0.854								
B3	0.855	0	0	0	0	0	0	0	GC
B4	0.943	30	30	100	85	233	318	7.8	GC/MS
B5	0.913								
B6	0.916	30	30	210	20	300	320	7.8	GC
B7	0.913								
B9	0.923	30	29	100	90	220	310	13.5	GC
B10	0.924								
B11	0.921	30	30	202	30	280	310	13.5	GC
B12	0.910								
B13	0.900	30	30	209	26	280	306	13.5	GC/MS
B14	0.903								
B15	0.916	0	0	0	0	0	0	0	GC/MS

(continued)

Table 5 (cont'd.)

Cartridge	Tenax GC, grams	Air Sampled		Ozone Conc., ppb	Nitric Oxides		Conc., NO_x ppb	Water Vapor mm Hg	Analysis
		Vol., L	Time, Min		NO ppb	NO_2 ppb			
1	2	3	4	5	6	7	8	9	10
B16	0.916	30	30	0	0	0	0	0	GC
B17	0.914								
B18	0.914	30	29	0	0	0	0	0	GC/MS
B19	0.908								
B20	0.919	0	0	0	0	0	0	0	GC
B21	0.912								

Table 6. PEAKS DETECTED BY TOTAL ION CURRENT MONITORING ($O_3/NO_x/H_2O$)

Cartridge	Column	Retention Time, min			
B15 (blank)	CW20M	6.23(100)	7.90(39.5)	10.33(-)	13.70(-)
		15.87(-)	22.17(-)	27.33(13)	41.33(37.8)
B4	CW20M	8.20(25)	11.90(10)	17.27(-)	21.63(-)
		24.86(-)	28.33(26)	30.67(45.2)	35.50(100)
		42.00(63.8)	43.80(21)		
B13	CW20M	28.61(20.3)	31.12(43.5)	35.66(100)	
		42.61(54.2)	45.01(22.6)		
B18 (blank)	CW20M	4.30(100)	10.36(-)	17.17(-)	21.40(-) 26.00(13)
		30.00(-)	32.70(8.5)	34.93(3.9)	
		37.27(-)	39.67(75.7)		
B5	OV-101	7.10(10.7)	12.37(39.5)	14.50(-)	18.67(-)
		20.46(42.4)	22.77(21.5)	27.33(62.7)	31.93(-)
		37.63(-)	44.63(-)	48.17(-)	53.63(-)
		60.2(100)			
B14	OV-101	4.33(16.9)	5.77(13)		
		7.00(20.9)	9.00(-)	10.53(-)	12.70(42.4)
		14.30(-)	17.23(11.3)	20.26(63.8)	21.50(-)
		22.57(198)	25.70(-)	26.97(100)	28.27(7.3)
		31.77(-)			
B19 (blank)	OV-101	3.16(91.5)	4.50(14.1)	6.03(100)	7.03(27.1)
		7.90(-)	9.67(-)	12.27(35.0)	13.53(-) 15.00(-)
		17.30(-)	18.43(-)	20.39(-)	22.70(72.3) 24.53(-)
		26.10(-)	27.47(11.3)	28.73(-)	30.70(-)
		60.00(79.4)	72.33(31.6)		

Table 7. MASS SPECTRAL DATA FOR MAJOR PEAKS ($O_3/NO_x/H_2O$)

Compound	Retention Time, Min[a]	m/z (Rel. Int.)
ethylene oxide	6.30/-	42.00(10.64); 43.00(58.05); 44.00(100.00)
acetic acid	28.47/12.53	42.00(3.39); 43.00(95.80); 44.00(16.12); 45.00(100.00), 60.00(36.65)
benzaldehyde	30.40/20.36	37.00(2.92); 38.00(2.59); 39.00(2.92); 44.00(13.61); 50.00(32.77); 51.00(48.50); 61.00(2.00); 74.00(1.67); 77.00(100.00); 78.00(10.35); 104.00(1.92); 105.00 (93.49); 106.00(79.22)
acetophenone	35.58/27.15	39.00(2.04); 42.00(4.49); 43.00(28.62); 44.00(0.99); 50.00(14.01); 51.00(37.54); 52.00(0.78); 62.00(0.7); 74.00(1.29); 76.00(1.08); 77.00(81.08); 78.00(1.14); 91.00(0.60); 105.00(100.00); 120.00(17.25); 121.00(0.1)
phenol	42.30/-	39.00(25.25); 40.00(36.36); 44.00(15.82); 55.00(11.78); 57.00(3.87); 65.00(16.33); 66.00(43.27); 94.00(100.00)

[a]Mean of two values, CW 20M/OV-101 columns.

External Standard Calibration of Gas Chromatography Analysis System--

For the quantitative analysis of the main Tenax GC decomposition products - benzaldehyde, acetophenone, and phenol - an external calibration of the GC system was performed. Cartridges were loaded with standards from methanolic solution standards or by using permeation tubes.

Sample chromatograms for cartridges loaded with the "flash-evaporation" system and the permeation system are presented in Figures 5 and 6, respectively. These analyses were performed by thermal desorption/high resolution gas chromatography (TD/HRGC).

For each calibration run a K value was calculated for the compound of interest:

$$K = \frac{Q\ (ng)}{A_{meas}\ (a.u.)}$$

Q = quantity of standard loaded, ng
A_{meas} = peak area, arbitrary units

The peak areas actually measured by the CDS-111C integrator were converted to normalized values:

$$A = A_{meas} \times \frac{\text{Sensitivity}}{10^{-12}} \times \text{attenuation}$$

To test for outliers, a Student t test was used.[11] For the suspected value, XD, a t value was calculated from the relationship:

$$t = \frac{X_D - \bar{X}}{S\sqrt{\frac{n}{n-1}}}$$

$\bar{X}$ = mean of n values (excluding X_D);
S = standard deviation for n values;
n = number of GC calibration runs for compound of interest.

If $t \geq t_{crit.}$ ($\upsilon = n-1$; $\alpha = 0.05$) X_D is excluded from the calculated mean. The next extreme value was tested, until the t test was negative. The analytical data used for K calculations and the final K values are presented in Tables 8, 9, and 10.

Factorial Experiment 2^3: Ozone-Nitric Oxides - Humidity--

The parameters and their level in the 2^3 factorial experiment are listed in Table 11.

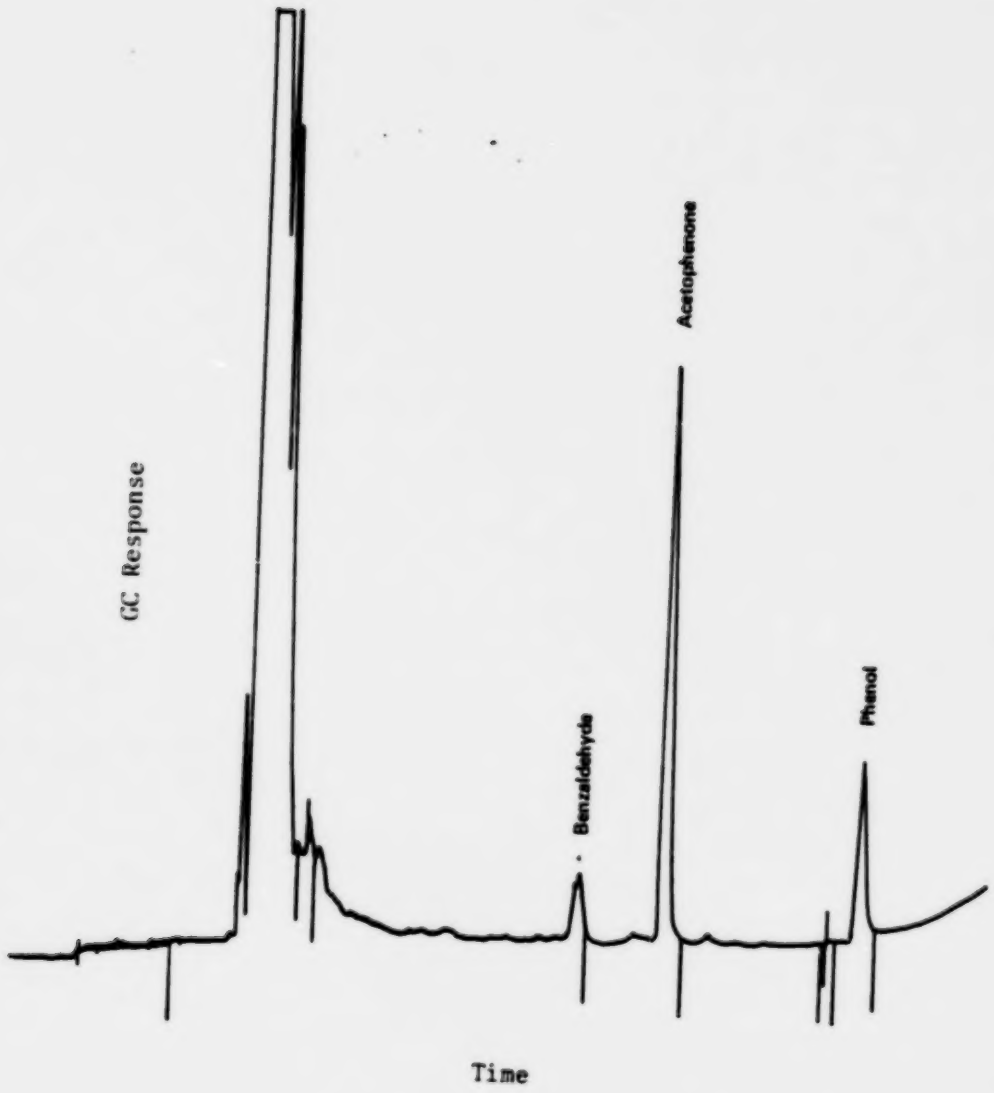


Figure 5. TD/HRGC analysis of a Tenax GC cartridge loaded with MeOH solution of standards.

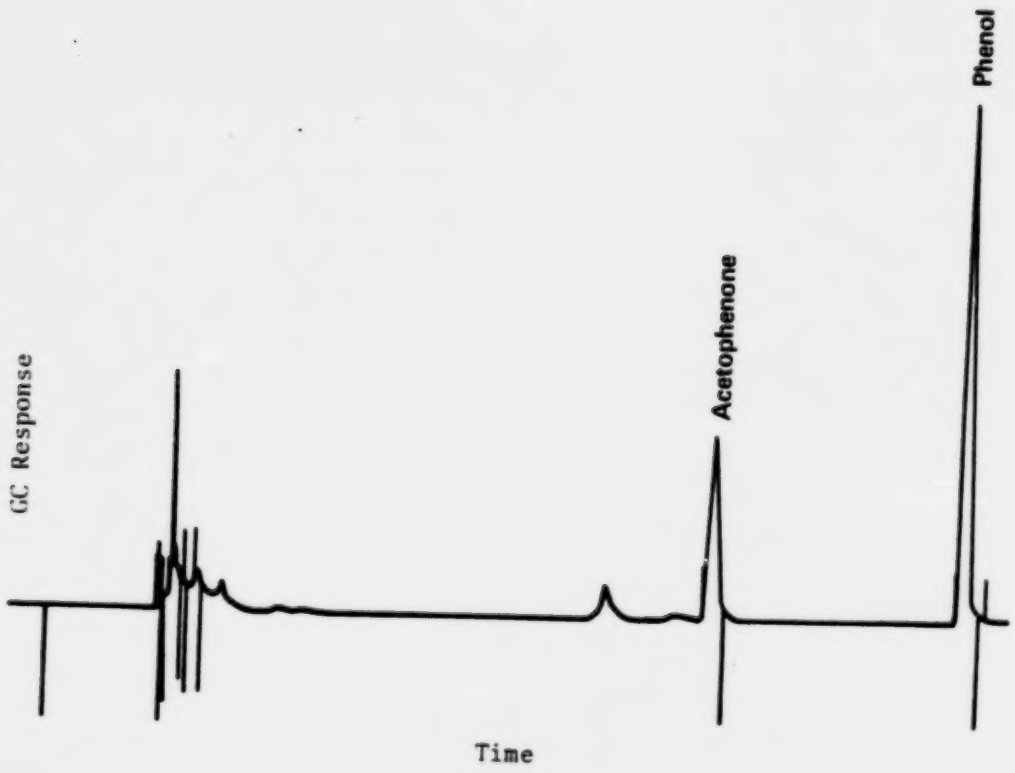


Figure 6. TD/HRGC analysis of a Tenax GC cartridge loaded with the permeation system.

Table 8. EXTERNAL STANDARD CALIBRATION FOR BENZALDEHYDE

No.	GC Run ID	Q, ng x 10^3	A x 10^{-6} A.U.	K x 10^{-6}	Loading Method[a]
1	217.01	46.2	213.6	216	A
2	216.05	48.1	218.7	220	A
3	217.02	18.9	62.9	300	A
4	217.03	17.9	47.7	375	A
5	217.04	18.4	51.4	358	A
6	217.05	8.02	27.6	291	A
7	218.01	8.96	24.0	373	A
8[b]	718.02	3.77	7.1	530	A
9	718.03	4.72	17.8	265	A

$\bar{K}$ = 300
n = 8
SD = 64

[a]A = from methanol solutions; B = with the permeation system.
[b]Outlier, t test positive.

Table 9. EXTERNAL STANDARD CALIBRATION FOR ACETOPHENONE

No.	GC Run ID	Q, ng x 10^3	A x 10^{-6} A.U.	K x 10^{-6}	Loading Method[a]
1	217.02	17.5	80.5	217	A
2	217.03	16.6	64.7	257	A
3	217.04	17.1	64.1	268	A
4	217.05	7.45	34.7	215	A
5	218.01	8.33	28.8	289	A
6	218.03	3.5	6.7	522	A
7	218.03	4.4	19.8	222	A
8	218.04	0.89	3.11	286	B
9	218.05	0.89	2.03	438	B
10	219.01	0.45	1.12	402	B
11[b]	219.02	0.31	0.50	620	B
12	219.03	0.48	1.16	404	B
13[b]	219.05	0.17	0.25	680	B

$\bar{K}$ = 321
n = 11
SD = 105

[a]A = from methanol solutions; B = with the permeation system.

[b]Outlier, t test positive.

Table 10. EXTERNAL STANDARD CALIBRATION FOR PHENOL

No.	GC Run ID	Q, ng x 10^3	A x 10^{-6} A.U.	K x 10^{-6}	Loading Method[a]
1	217.02	26.7	83.1	321	A
2	217.03	25.3	49.4	512	A
3	217.04	26.0	51.1	509	A
4	217.05	11.3	35.3	320	A
5	218.01	12.7	3.5	378	A
6[b]	218.02	5.34	6.0	890	A
7	218.03	6.67	25.1	266	A
8	218.04	2.00	5.64	355	B
9	218.05	2.00	2.90	690	B
10	219.01	1.00	2.54	394	B
11	219.03	1.06	2.81	377	B
12	219.05	0.38	0.73	520	B

$\bar{K}$ = 461
n = 11
SD = 123

[a]A = from methanol solutions; B = with the permeation system.
[b]Outlier, t test positive.

Table 11. FACTORS AND LEVELS IN THE 2^3 FACTORIAL EXPERIMENT: OZONE - NITRIC OXIDES - HUMIDITY

Factor	Level	
	Low	High
Ozone Concentration, ppb	100	200
Nitric Oxides Concentration, ppb	150	300
Humidity, % Relative at 23°C	40	80

The K values listed in Tables 8, 9, and 10 were used to quantitate benzaldehyde, acetophenone, and phenol. The analytical data are listed in Table 12.

Chromatograms of blank (unexposed), blank (exposed), and exposed Tenax GC cartridges are depicted in Figures 7, 8, and 9, respectively.

A Student t test was used to ascertain if the difference between blank exposed and blank unexposed cartridges was statistically significant. A t value was calculated from:

$$t = \frac{\bar{X}_1 - \bar{X}_2}{\bar{S}\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}}$$

for: $X_1^1, X_2^1, \ldots X_{n_1}^1$ values with $\bar{X}_1$ as mean and S_1 as SD;

$X_1^2, X_2^2, \ldots X_{n_2}^2$ values with $\bar{X}_2$ as mean and S_2 as SD;

$$S = \frac{(n_1-1)S_1^2(n_2-2)S_2^2}{n_1 + n_2 - 2}$$

t was compared to $t_{crit.}$ ($\upsilon = n_1 + n_2 - 2$ degrees of freedom, $\alpha = 0.05$).

$$|t| < |t_{crit}| \text{ , then } \bar{X}_1 \sim \bar{X}_2$$

$$|t| > |t_{crit}| \text{ , } \bar{X}_1 = \bar{X}_2$$

The results of the test are presented in Table 13. No statistically significant difference was found between blank exposed and blank unexposed cartridges. This result is important, since it establishes that the experimental system is reasonably free from contamination.

The same test was performed for the blank cartridges (exposed and unexposed) versus the pair of cartridges exposed to the lowest level of oxidants and humidity.

Table 12. BENZALDEHYDE, ACETOPHENONE, AND PHENOL DESORBED FROM TENAX GC (EXPOSED AND BLANK) CARTRIDGES

Cartridge ID[a]	GC Run ID	Benzaldehyde		Acetophenone		Phenol	
		A x 10^{-6}	Q, ng	A x 10^{-6}	Q, ng	A x 10^{-6}	Q, ng
A2	122.01	4.28	1,280	1.16	370	2.40	1,010
A3	122.02	1.75	530	0.61	200	0.65	270
A5	124.02	13.38	4,010	3.13	1,010	8.23	3,470
A6	122.03	0.22	70	0.07	20	0.05	20
A7	124.03	15.20	4,560	31.36	10,100	24.32	10,300
A8	124.04	23.44	7,030	7.61	2,440	11.90	5,020
A9	125.01	38.54	11,560	10.14	3,250	23.26	9,810
A11	122.02	0.21	60	0.11	40	0.06	30
A12	125.03	0.76	230	0.41	130	0.21	90
B2	123.02	2.73	670	0.94	300	1.16	490
B7	125.04	38.85	11,650	12.25	3,930	24.02	10,140
B8	125.05	0.90	270	0.47	150	0.07	30
B9	128.02	43.55	13,070	12.48	4,010	29.48	12,440
B10	128.03	50.37	15,110	14.89	4,780	31.62	13,340
B11	125.06	12.03	3,610	4.44	1,425	4.77	2,010
B12	128.01	45.33	13,600	15.50	4,980	77.54	11,620
B16	129.01	0.28	80	0.15	50	0.11	50
B17	129.02	0.79	220	0.41	130	0.12	50
B20	129.03	0.21	60	0.14	50	0.06	30

[a]Refer to Table 5 for experimental parameters employed for each cartridge.

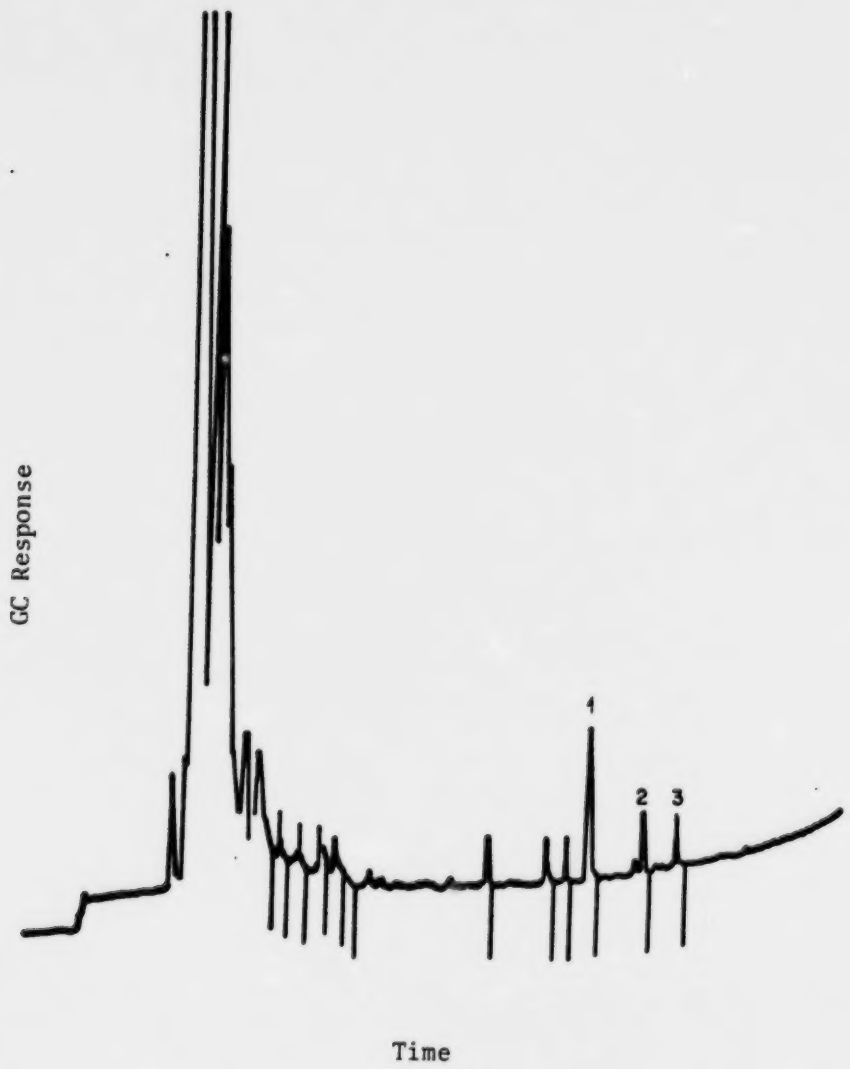


Figure 7. Blank (unexposed) Tenax GC cartridge TD/HRGC analysis: (1) benzaldehyde; (2) acetophenone; and (3) phenol.

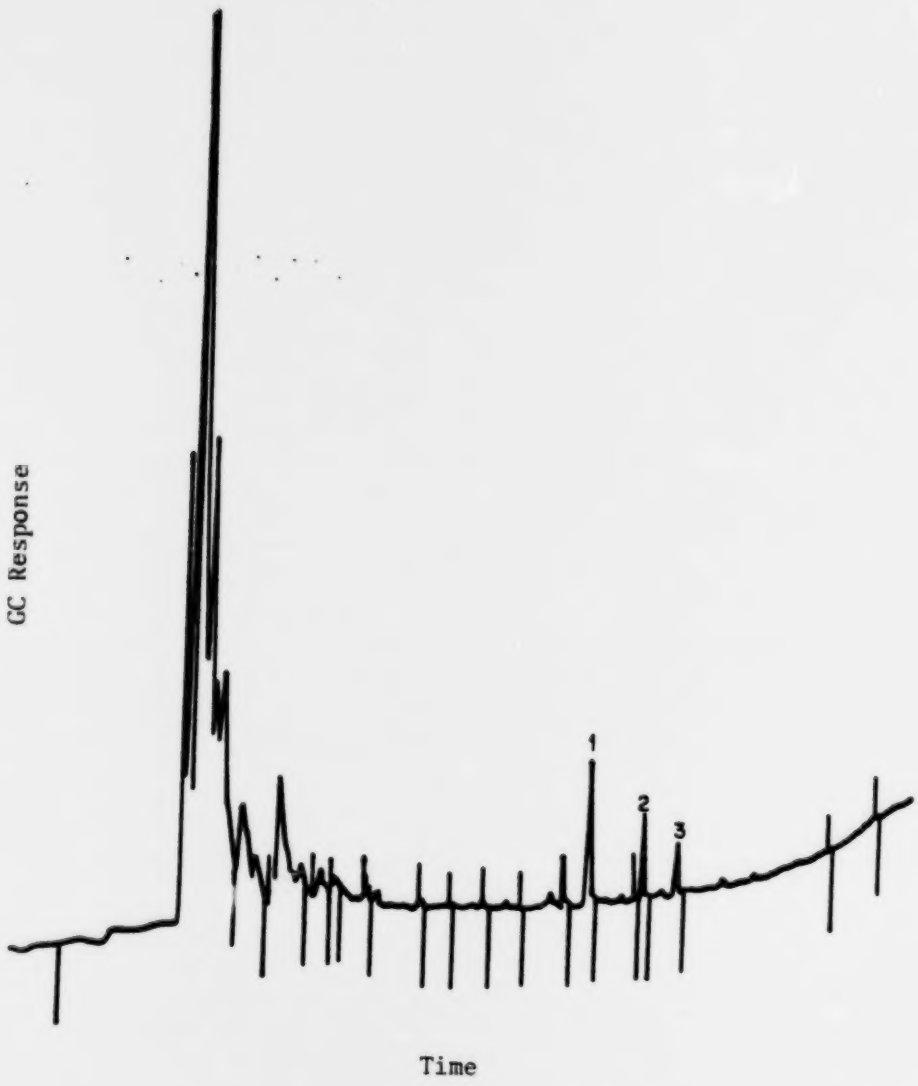


Figure 8. Blank (exposed) Tenax GC cartridges TD/HRGC analysis: (1) benzaldehyde; (2) acetophenone; and (3) phenol.

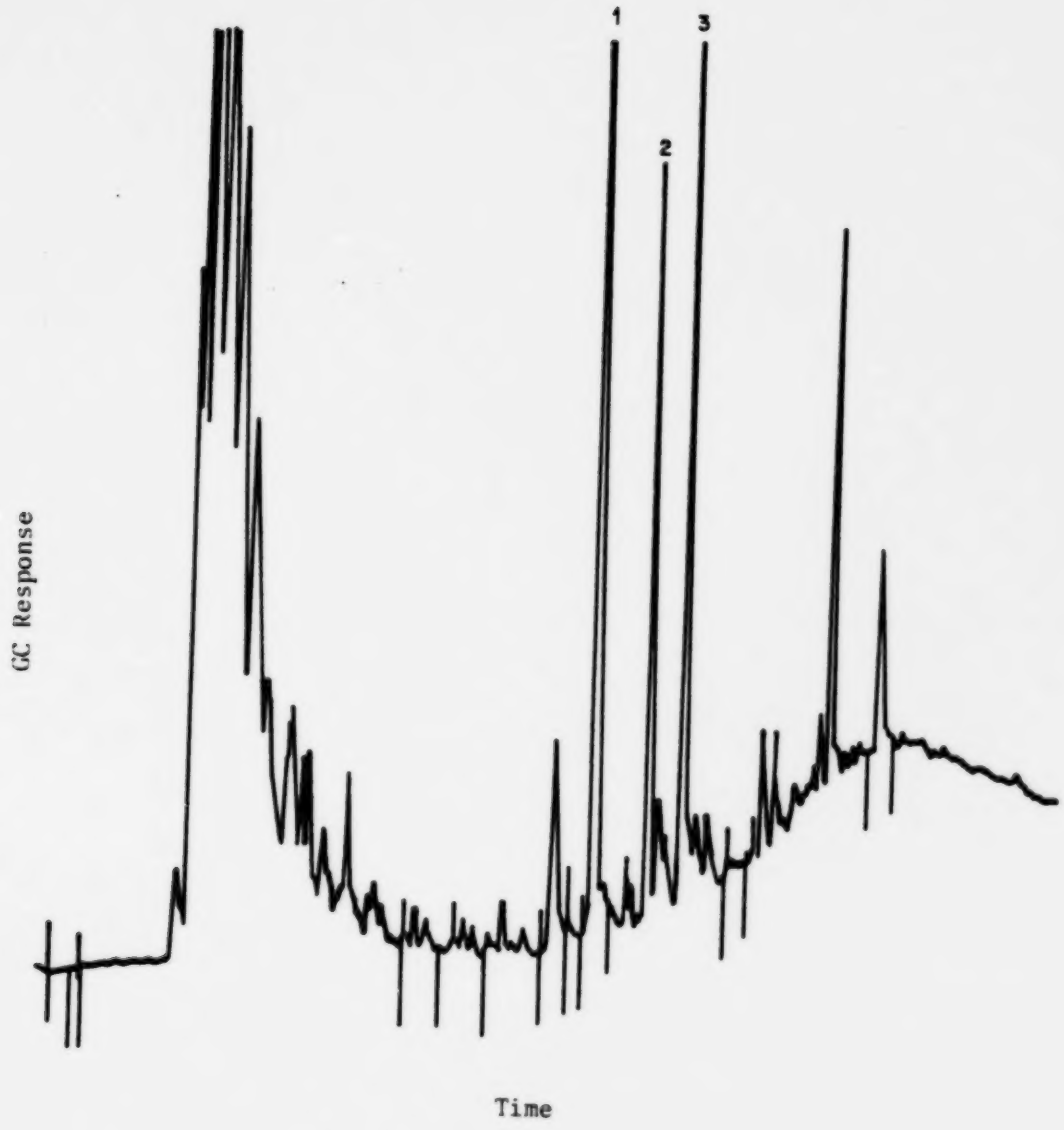


Figure 9. Exposed Tenax GC cartridges TD/HRGC analysis: (1) benzaldehyde; (2) acetophenone; and (3) phenol.

Table 13. STUDENT t TEST FOR BLANK TENAX GC CARTRIDGES

	Ng/Cartridge			
	Benzaldehyde	Acetophenone	Phenol	All Three
Blank, unexposed	20 270 145 ± 125	20 150 85 ± 92	20 30 25 ± 7	110 450 280 ± 240
Blank, exposed	60 230 60 117 ± 98	40 130 50 73 ± 49	30 90 30 50 ± 35	130 450 140 240 ± 182
$\bar{S}$	114	66	79	203
t	0.40	0.199	0.944	0.216
$\bar{x}$ (n=5)	138 ± 103	78 ± 58	40 ± 78	256 ± 177

t_{crit} (υ = 3; α - 0.05) = 3.182.

The results of the test are presented in Table 14. The difference between exposed cartridges (low level) and blank cartridges was statistically significant at a confidence level higher than 98% or 95%. The matrix of data from 2^3 factorial experiment is presented in Table 15. The estimation of variance in the data matrix was possible, even if not all the measurements were in duplicate, by using the relationship[8]:

$$S^2 = \sum_1^n \frac{di^2}{2n} = \frac{1}{2n} \sum_1^n d_1^2$$

The variance and standard deviation of the study results were calculated in terms of observed effect as follows:

$$V_{effect} = \frac{4}{N} S^2 \qquad N = \text{number of runs}$$

$$S_{effect} = \sqrt{V_{effect}}$$

The following values were obtained:

$$S_{effect} = \frac{\text{Benzaldehyde}}{1250} + \frac{\text{Acetophenone}}{445} + \frac{\text{Phenol}}{1260} = \frac{\text{Sum of Three}}{2955}$$

Somewhat arbitrarily, we defined an effect $\geq 2 \cdot S_{effect}$ significant. The effects of the three parameters and their interactions are listed in Table 16. The relationships for calculating the effects and interactions were:

Main Effects

$$\text{ozone} = \frac{y_2 + y_4 + y_6 + y_8 - y_9 - y_3 - y_5 - y_7}{4}$$

$$NO_x = 1/4\ (y_3 + y_4 + y_7 + y_8 - y_1 - y_2 - y_5 - y_6)$$

$$\text{Humidity} = 1/4\ (y_5 + y_6 + y_7 + y_8 - y_1 - y_2 - y_3 - y_4)$$

Interactions

$$\text{Ozone} \times NO_x = 1/4\ (y_1 + y_4 + y_5 + y_8 - y_2 - y_3 - y_6 - y_7)$$

$$\text{Ozone} \times \text{Humidity} = 1/4\ (y_1 + y_4 + y_5 + y_8 - y_2 - y_3 - y_6 - y_7)$$

$$\text{Ozone} \times NO_x \times \text{Humidity} = 1/4\ (y_2 + y_3 + y_5 + y_2 - y_1 - y_4 - y_6 - y_7)$$

Table 14. STUDENT t TEST FOR BLANK AND LOW LEVEL EXPOSED TENAX GC CARTRIDGES

	ng/Cartridge ± S.D.			
	Benzaldehyde	Acetophenone	Phenol	All Three
Blank Cartridges	183 ± 103	78 ± 58	40 ± 28	256 ± 177
A_2, A_3 (low level)	905 ± 530	285 ± 120	640 ± 523	1830 ± 1174
$\bar{S}$	254	75	235	548
t	3.608	3.297	3.042	3.432

α(CL):	0.05(95)	0.02(98%)	0.01(99%)
t_{crit} (υ=5)	2.571	3.365	4.032

Table 15. DATA MATRIX FOR FACTORIAL EXPERIMENT 2^3: OZONE - NITRIC OXIDES - HUMIDITY

Cartridge	Ozone	NO_x	Humidity	ng/Cartridge ± S.D.			
				Benzaldehyde	Acetophenone	Phenol	All Three
$A_2, A_3(y_1)$	-	-	-	905 ± 375	285 ± 85	640 ± 370	1,830 ± 830
$A_4(y_2)$	+	-	-	4,010	1,010	3,470	8,490
$B_2(y_3)$	-	+	-	670	300	490	1,460
$B_7(y_4)$	+	+	-	11,650	3,930	10,140	25,720
$A_9(y_5)$	-	-	+	11,560	3,250	9,810	24,620
$A_7, A_8(y_6)$	+	-	+	5,795 ± 1,235	6,270 ± 3,830	7,660 ± 2,640	19,725 ± 5,235
$B_9, B_{10}(y_7)$	-	+	+	14,090 ± 1,020	4,395 ± 385	12,890 ± 450	31,375 ± 1,855
$B_{11}, B_{12}(y_8)$	+	+	+	8,605 ± 4,995	3,200 ± 1,780	6,815 ± 4,805	18,620 ± 11,580

Table 16. MAJOR EFFECTS AND INTERACTIONS CALCULATED FOR THE FACTORIAL EXPERIMENT 2^3: OZONE - NITRIC OXIDES - HUMIDITY

Main Effect Of	ng/Cartridge ± S.D.			
	Benzaldehyde	Acetophenone	Phenol	All Three
Ozone	0	1500 ± 450	0	0
NO_x	3190 ± 1250	0	2200 ± 1200	5600 ± 2900
Humidity	5700 ± 1250	2900 ± 450	5600 ± 1200	14200 ± 2900
Interactions				
Ozone x NO_x	0	0	0	0
Ozone x Humidity	-6300 ± 1250	0	-5200 ± 1200	-12150 ± 29
NO_x x Humidity	0	-1200 ± 450	0	0
Ozone x NO_x x Humidity	0	-1800 ± 450	-2700 ± 1200	-6400 ± 29

The main effect was the difference between two averages:

$$\text{main effect} = \bar{y}+ = \bar{y}-$$

Where $\bar{y}+$ is the average response for the + level of the variable, and $\bar{y}-$ is the response for the - level of the variable. The interactions are measures of non-additivity of the main effects. They are differences between averages of parameter "a" effect at level + and - for parameter "b" (halved by convention).

The major effects and interactions for the factorial experiment are listed in Table 16. The experiment had explored a region in which a combination of high concentration of oxidants and high relative humidity tends to reduce somewhat the quantities of the three dosed decomposition products, by decomposing them faster than they were generated from the polymer (negative sign for all significant interactions).

Humidity played a very important role. This is important since more attention should be given to artifact formation of Tenax GC when sampling air with a high relative humidity.

The ozone concentration and NO_2 concentration behaved additively, i.e., the total concentration of oxidants in air was very important for artifact production. The three major decomposition products of Tenax GC are found in easily detectable and dosable quantities even in "clean" cartridges. Benzaldehyde, acetophenone, and phenol are common decomposition products of Tenax GC. It appears that analysis for any of these three compounds at levels below 100 ng/L with Tenax GC sampling is <u>not</u> possible without special precautions.

Effects of Sulfur Oxides

Tenax GC cartridges were exposed to 30 L air with ozone, sulfur oxides, and nitric oxides at different humidity levels. The relevant information regarding the exposed cartridges is listed in Table 17.

One cartridge exposed to the highest levels of reactive compounds was analyzed by GC/MS; the total ion current chromatogram is presented in Figure 10, and the INCOS library search peak identification is listed in Table 18. The major Tenax GC decomposition products were confirmed (benzaldehyde,

Table 17. ARTIFACT FORMATION BY TENAX GC ITSELF: $O_3/NO_x/SO_x/H_2O$

Cartridge	GC,ID	Air Sampled L	Conc., ppb			Humidity %	Ph-CHO	Ph-COCH	Ph-OH	Observation
			O_3	NO_x	SO_x					
B17	085-01	0	0	0	0	0	ND[a]	ND	ND	blank unexposed
C1	085-06	30	0	0	0	60	30	ND	20	blank exposed
B1	085-02	30	100	150	0	60	65	20	60	control
B9	085-03	30	100	150	100	60	105	30	125	
B11	-	30	100	150	100	60	-	-	-	GC/MS
B12	085-04	30	100	0	100	60	40	ND	20	
B20	085-05	30	100	0	200	60	40	10	30	

[a]ND = Not detected, values are in ng.

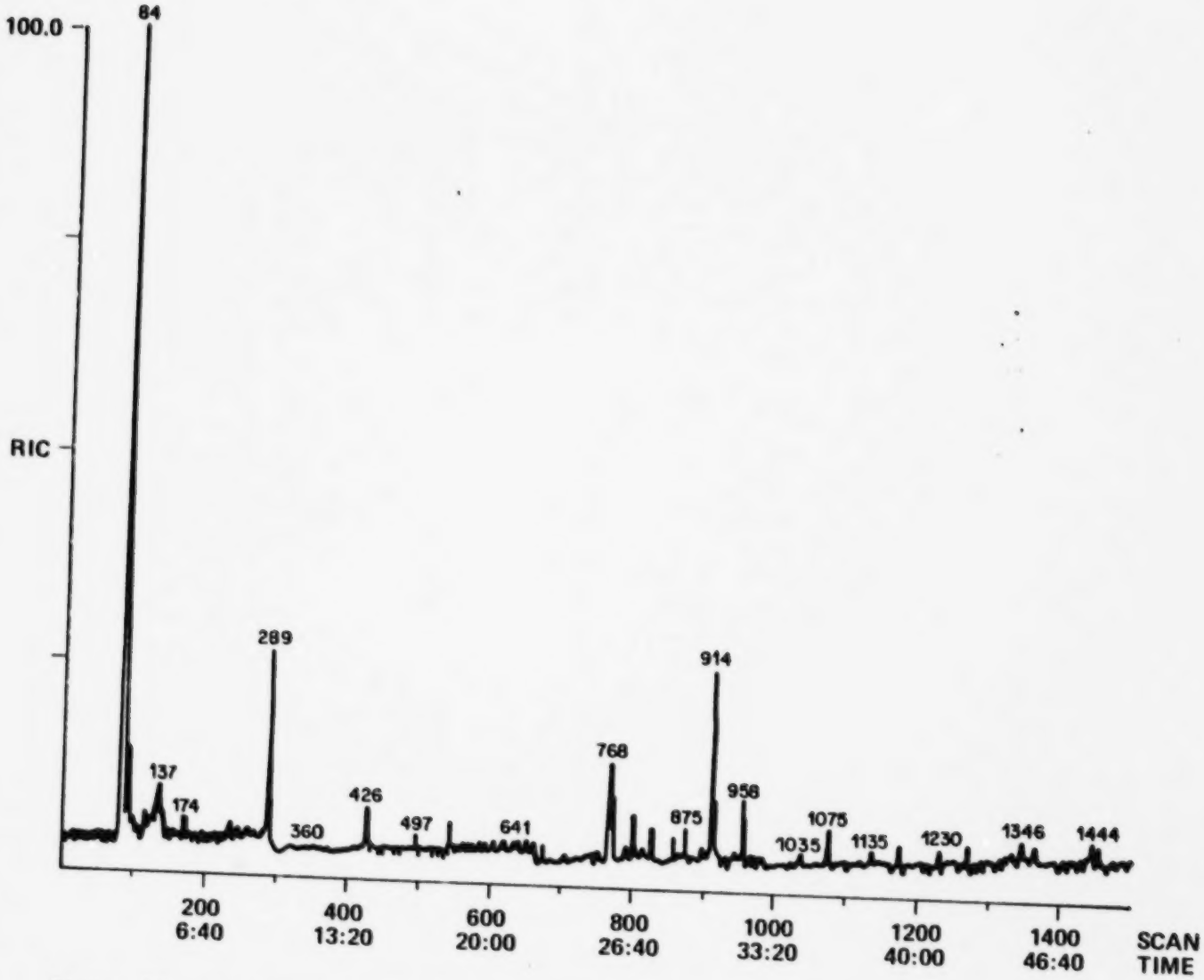


Figure 10. TIC chromatogram for a Tenax GC exposed cartridge ($O_3/NO_x/SO_x/H_2O$).

Table 18. COMPONENTS IDENTIFIED FROM TENAX GC CARTRIDGE EXPOSED TO: $O_3/SO_x/NO_x/H_2O$

Scan No.	RRT	Compound	Observation
137	0.15	methylene chloride	contamination
289	0.32	trichloroethylene	contamination
426	0.47	toluene	contamination
497	0.54	C_8H_{18} hydrocarbon	contamination
545	0.60	siloxane	column bleeding (?)
677	0.74	hydrocarbon	contamination
768	0.84	benzaldehyde	artifact/Tenax GC
806	0.88	phenol	artifact/Tenax GC
914	1.00	acetophenone	artifact/Tenax GC
802	0.88	benzonitrile	questionable ID
958	1.05	nonanal	questionable ID

acetophenone and phenol), while no compounds specific for the presence of sulfur oxides could be detected.

Effects of Chlorine

Tenax GC cartridges were exposed to ozone, chlorine, humidity, and analyzed by TDHR-GC and GC/MS methods. Experimental parameters and the quantities of benzaldehyde, acetophenone, and phenol formed (calculated with the K values generated by external standarization) are listed in Table 19.

The gas chromatogram for an exposed Tenax GC cartridge is presented in Figure 11. The total ion current (TIC) chromatogram of a GC/MS analyzed cartridge is presented in Figure 12, and the INCOS library search identifications for the major peaks are listed in Table 20. Again, the same major decomposition products - benzaldehyde, acetophenone, and phenol - were found. A characteristic change in the ratio between products was observed; much more acetophenone was formed in this case.

Effects of Tenax GC Aging

For all data related to SO_x and Cl_2 present in the "sampled" air, substantially less decomposition products were found. This effect was not related to the nature of reactive inorganic gases (in all experiments ozone was present, which is the main factor in polymer degradation), but to the "history" of the Tenax GC cartridge.

In the SO_x and Cl_2 series of experiments, recycled Tenax GC cartridges were used. The hypothesis that the history of cartridges was the main factor in the total quantity of degradation products was tested using the same cartridge, exposed to 30 L air in 30 min, with 100 ppb ozone, 150 ppb NO_x and 60% humidity. The quantities of Tenax GC degradation products are listed in Table 21, together with specific surface area measurements by mercury intrusion porosimetry for the "virgin" sorbent and sorbent after five analysis cycles.

The quantities of degradation products decreased by an order of magnitude after five analysis cycles. The specific surface area decreased slightly (may not be statistically significant) but definitely not enough to explain this phenomenon.

Table 19. QUANTIFIED COMPONENTS FROM TENAX GC ITSELF: $Cl_2/O_3/H_2O$

Cartridge	GC-ID	Air Sampled, L	Conc., ppb		Humidity %	Q, ng of			Observations
			Cl_2	O_3		Ph-CHO	Ph-$COCH_3$	Ph-OH	
A1	5/12/81/2	30	0	0	60	ND[a]	ND	ND	blank exposed
A2	5/12/81/3	30	117	0	60	ND	ND	ND	
A4	5/12/81/4	30	117	150	60	ND	5	ND	
A6	5/12/81/5	30	173	200	60	6	40	10	
A7	-	30	173	200	60	-	-	-	GC/MS

[a]ND = not detected.

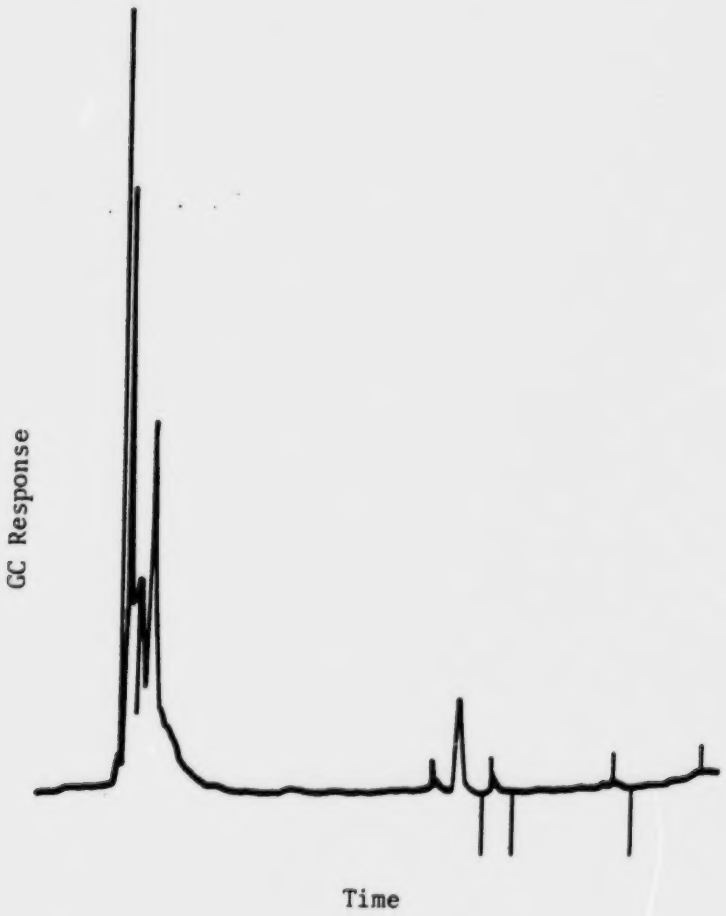


Figure 11. TD/HRGC analysis of a Tenax GC exposed cartridge ($Cl_2/O_3/H_2O$).

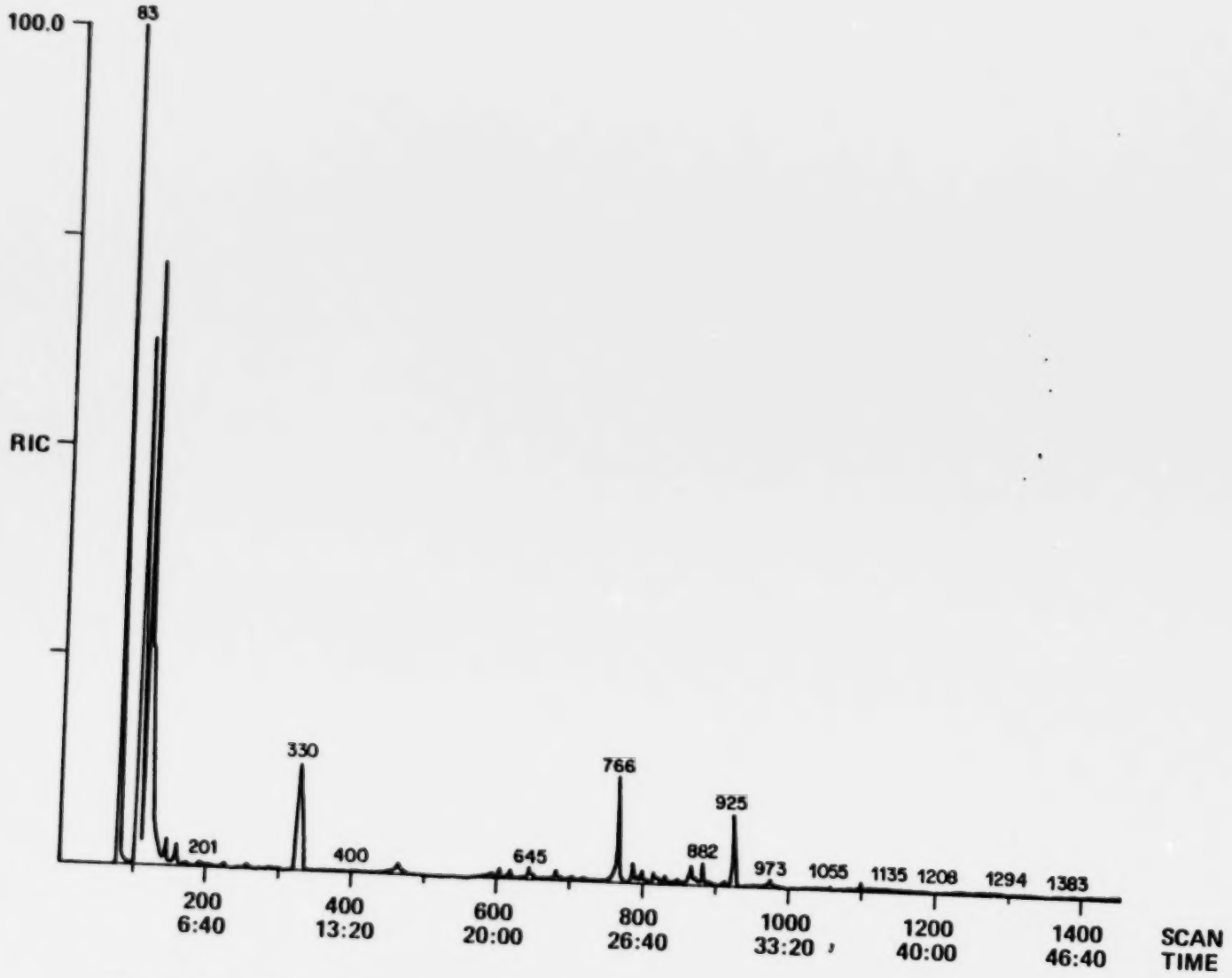


Figure 12. TIC chromatogram for a Tenax GC exposed cartridge ($Cl_2/O_3/H_2O$).

Table 20. COMPONENTS IDENTIFIED FROM TENAX GC CARTRIDGE EXPOSED TO $Cl_2/O_3/H_2O$

Scan Number	RRT	Compound	Observations
107	0.12	Freon II	Contamination
117	0.13	Acetone	Contamination
117	0.13	1,1,2-Trichloro-1,2,2-trifluoroethane	Contamination
145	0.16	Hexane	Contamination
191	0.21	Benzene	Contamination
330	0.36	Toluene	Contamination
464	0.50	Siloxane	Column bleeding (?)
761	0.82	Benzaldehyde	Artifact/Tenax GC
766	0.83	Hydrocarbon	Contamination
925	1.00	Acetophenone	Artifact/Tenax GC

Table 21. QUANTIFIED COMPONENTS FROM TENAX GC ARTIFACT FORMATION

Cartridge	Sorbent Specific Surface Area, m^2/g[a]	Degradation Products, ng/cartridge		
		Ph-CHO	$Ph-COCH_3$	Ph-OH
B1, cycle #1	69.5	670	300	490
B1, cycle #5	62.6	65	20	60

[a]By mercury intrusion porosimetry, analysis performed by "Quatachrome".

A more probable explanation is that the sorbent surface was depleted in readily degradable oligomers by repeated oxidation/thermal desorption.

ARTIFACT PRODUCTS FROM REACTIONS OF ADSORBED COMPOUNDS

Experimental Procedures

Tenax GC cartridges (60 mm length x 13 mm diameter sorbent bed) were loaded with d_{10}-cyclohexene or d_5-ethanol. For quantitation, 2-fluorobiphenyl was used as an internal standard. Standard solutions of cyclohexene-d_{10} (Merck Sharp & Dohme Canada, Ltd., 99% D) and 2-fluorobiphenyl (Pfaltz & Bauer, MW 172, bp 248°C) were prepared by weighing (Mettler Microbalance) and dissolving in pure (redistilled, distilled in glass) methanol in a volumetric flask.

Tenax GC cartridges were loaded with cyclohexene-d_{10} (1,000-2,000 ng) using the experimental setup presented in Figure 4. The flow rate of purified helium (activated charcoal trap and cryogenic trap) was 75 mL/min. A volume of 5 to 10 µL of the cyclohexene-d_{10} standard solution was injected (Hamilton 701 N microsyringe) through the silicone rubber septum into the glass bulb. The Tenax GC cartridge was kept in the helium stream ca. 10 min.

The loaded cartridges were exposed, using the experimental setup presented in Figure 1, to an air flow containing inorganic gases (potential generators of artifacts by reaction with the adsorbed cyclohexene-d_{10}):

- chlorine: max. conc. 564 ppb;
- ozone: max. conc. 1,000 ppb;
- NO/NO_2: max. conc. 500 ppb;
- SO_2/SO_3: max. conc. 400 ppb;
- humidity: 50% at 25°C

In the third step 2-fluorobiphenyl was loaded onto the Tenax GC cartridge with the same setup presented in Figure 4.

Finally, the Tenax GC cartridge was analyzed by TD-HRGC using the experimental parameters listed in Table 22. Duplicate cartridges were analyzed by GC/MS employing the experimental parameters listed in Table 4. Some cartridges were analyzed using an LKB 2091 instrument (see Table 26).

Pertinent information related to loading with d_{10}-cyclohexene, exposing, and analysis of Tenax GC cartridges is listed in Table 23.

Table 22. EXPERIMENTAL PARAMETERS FOR THERMAL DESORPTION - HIGH RESOLUTION GAS CHROMATOGRAPHY OF TENAX GC CARTRIDGES LOADED WITH DEUTERATED COMPOUNDS

Parameter	Conditions, etc.
Instrument	Varian 3700 GLC, FID detector
Thermal Desorption	8 min/270°C; 10 mL/min helium purge; 4.5 min injection; cryogenic trap temperature raised from -196°C to 250°C
Column	50 m fused silica, wide bore capillary, stationary phase SE-54.
Temperature Program	40°C/10 min; 40 to 250°C at 4°C/min; 250°C/10 min
FID Electrometer output	10^{-11} AFS x 1, 2 or 4 (Att.)

Table 23. ARTIFACT STUDIES USING d_{10}-CYCLOHEXENE

Cartridge	GC Run	ID	Loaded With (ng)		Air Sampled			Inorganic Gases	Remarks
			C_6D_{10}	IS[a]	Flow L/min	Time min	Vol. L		
B8	5/13/81	#9	1,058	500	0.05	15	7.5	Cl-282 ppb 50% humidity	
B12	5/14/81	#14	1,058	500	0.5	30	15	"	Duplicate Cl to GC/MS
B17	5/14/81	#15	1,058	500	0.5	45	22.5	"	
C6	5/19/81	#30	1,058	500	0.5	30	15	Cl_2 282 ppb O_3 5 ppb, 50% hum.	
C7	5/19/81	#29	1,058	500	0.5	30	15	Cl_2 282 ppb, O_3 100 ppb, 50% hum.	A1/GC/MS
B9	5/29/81	#4	1,058	500	0.25	60	15	Cl_2 565 ppb O_3 50 ppb 50% hum.	B10/GC/MS
B12	5/29/81	#6	2,116	500	0.25	60	15	"	B17/GC/MS
C2	6/01/81	#2	2,116	500	0.25	120	30	Cl_2 565 ppb O_3 40 ppb 50% hum.	A4/GC/MS
A4	5/20/81	#2	1,037	500	0.5	30	15	O_3 500 ppb 50% hum.	A6/GC/MS
B20	6/02/81	#6	2,116	500	0.5	30	15	O_3 1,000 ppb 50% hum.	B21/GC/MS

(continued)

Table 23 (cont'd.)

Cartridge	GC Run	ID	Loaded With (ng) C_6D_{10}	Loaded With (ng) IS[a]	Air Sampled Flow L/min	Air Sampled Time min	Air Sampled Vol. L	Inorganic Gases	Remarks
A8	5/20/81	#3	1,058	500	0.5	30	15	O_3 200 ppb NO_x 200 ppb 50% hum.	.B6/GC/MS
C4	6/03/81	#1	2,116	500	0.5	30	15	O_3 500 ppb NO 500 ppb NO_2 500 ppb 50% hum.	C5/GC/MS
A9	5/20/81	#4	1,037	490	0.5	30	15	NO 200 ppb NO_2 200 ppb 50% hum.	A10/GC/MS
A11	5/21/81	#1	1,058	500	0.5	30	15	O_3 135 ppb SO_2 335 ppb SO_3 65 ppb	BS/GC/MS

[a]IS = internal standard, 2-fluorobiphenyl.

For loading d_5-ethanol onto Tenax GC cartridges, the experimental setup presented in Figure 4 was used as a dilution system. The glass bulb was flushed with purified helium 25-30 min; the two Teflon stopcocks were closed and ca. 5 μL of d_5-ethanol were injected through the septum. After 1-1.5 min, the Teflon stopcocks were opened, and the glass bulb was flushed 15 min with helium (75 mL/min). The two stopcocks were closed again, and 5 μL of ethanol-d_5 injected through the septum. After approximately 2 min, 50 μL of gas were withdrawn from the glass bulb with a gas-tight Hamilton 1705 micro-syringe, and injected slowly into the middle of the Tenax GC cartridge. The reproducibility of the quantity of ethanol-d_5 loaded, as indicated by TD-HRGC of Tenax GC cartridges, was good.

The loaded Tenax GC cartridges were exposed to a flow of air containing ozone, NO_x, and humidity using the experimental set-up presented in Table 1. The parameters of the ethanol-d_5 experiments are listed in Table 24. Finally, the exposed Tenax cartridges were analyzed by TD-HRGC or GC/MS. The experimental conditions were identical to those previously listed except that a fused silica wide bore Carbowax 20M (Hewlett-Packard) and a 50°C/15 min; 50 to 190°C/12°/min temperature program were used. Compounds of interest for the present study eluted during the initial isothermal period. The very fast temperature programming which followed was only for "column cleaning".

d_{10}-Cyclohexene.

During the initial experiments with cyclohexene, stripping from Tenax GC cartridges was observed. Breakthrough volume data for cyclohexene-d_{10} on Tenax GC at ambient temperature were unavailable; however, by comparing data for related compounds [hexane, cyclohexane, hexane[12,13]], a breakthrough volume of 40-50 L of air was expected. Nevertheless, breakthrough of cyclohexene-d_{10} occurred for sampling volumes as low as 15 liters (see Table 25). The stripping of d_{10}-cyclohexene appeared to be time dependent, not volume dependent, which indicated a nonequilibrium desorption process. It is probable that the presence of humidity in the sampled air was one of the factors which was responsible for an early breakthrough. Recent studies have shown that the retention for some compounds on Tenax GC decreased as

Table 24. ARTIFACT STUDIES USING ETHANOL-d_5

Cartridge	GC Run	ID	EtOH-d_5 (ng/cart.)	Air, liters. . .with		Peak Height, mm	Sens x Att.
A5	6/1/81	1	3,200	0	0	235	10^{-10} x 1
D1	6/8/81	3	3,200	0	0	158	10^{-10} x 2
D3	6/8/81	5	3,200	0	0	156	10^{-10} x 2
D2	6/8/81	4	3,200	3.75	500 ppb O_3 500 ppb NO_x 50% humidity	39	10^{-10} x 2
B16	6/8/81	2	3,200	7.5	"	10	10^{-10} x 2
C7	for GC/MS Analysis		3,200	7.5	"	-	-
D6	for GC/MS Analysis		3,200	1.25	"	-	-

Table 25. STRIPPING OF CYCLOHEXENE-d_{10} FROM LOADED TENAX GC CARTRIDGES

Cartridge[a]	GC Run ID	Air Through the Cartridge			$h_{C_6D_{10}}/h_{IS}$[c]
		Flow L/min	Time min.	Vol. L	
B7	5/21/81/3	0	0	0	2.10
B3	5/29/81/2	0	0	0	1.74
B16	5/29/81/5	0	0	0	1.43
A2	6/01/81/3	0	0	0	1.48
A9	6/02/81/1	0	0	0	1.39
Mean ± SD (n=4)[b]					1.51 ± 0.16
A12	6/02/81/4	0.5	30	15	0.50
B7	6/02/81/5	0.5	30	15	0.51
A8	6/02/81/2	1	30	30	0.50
A11	6/02/81/3	1	30	30	
Mean ± SD (n=4)					0.50 ± 0.01

[a]Each cartridge loaded with 1,058 ng cyclohexene-d_{10} and 500 ng 2-fluorobiphenyl.

[b]Value for B7 excluded, Student t test positive (CL 90%).

[c]Peak heights ratio, d_{10}-cyclohexene/internal standard.

much as 50% with increasing humidity of the carrier gas[14,15]. The decrease was probably due mainly to stripping by the sampled air.

The random error in the analytical procedure was too high to differentiate loss by stripping from loss by chemical reaction. Thus, emphasis was devoted to identifying the compounds which originated through reactions of deuterated cyclohexane with inorganic reactive components in the sampled air by TD-HRGC and GC/MS.

The correspondence between GC and GC/MS analysis of duplicate cartridges is illustrated by the two chromatograms (FID and TIC detection) in Figure 13.

The results of a computer identification (INCOS software) of the components from exposed Tenax GC cartridges are listed in Table 26. The mass spectra obtained from an LKB 2091 instrument were manually interpreted[9,16], and the experimental data are listed in Table 27. Generally, there is an agreement between the two sets of data. Still, some INCOS software identifications were questionable (e.g., RRT 0.76 and 0.65). The TIC chromatograms for Tenax GC cartridges analyzed with an LKB 2091 instrument are presented in Figures 14 and 15.

For the low concentration range of reactive inorganic components in the sampled air, no deuterated cyclohexene product was detected. At higher chlorine concentrations, d_{10}-dichlorocyclohexane was found. A nondeuterated dichlorocyclohexane was also identified in the same samples, probably from chlorine reacting with cyclohexene (a contaminant). The nondeuterated compound eluted <u>after</u> the deuterated one. The nondeuterated 1,2-dichlorohexane was probably the <u>cis</u> isomer (bp $206\text{-}9^{762}$), while the deuterated compound was the trans, dl isomer (bp 189^{760}), a typical radical chain reaction product[17].

<u>d_5-Ethanol</u>

The gas chromatogram of an exposed Tenax GC cartridge is presented in Figure 16. The stripping of d_5-ethanol from the Tenax GC cartridge was by far the main factor responsible for the rapid loss from Tenax GC. Deuterated compounds derived from d_5-ethanol were not detected. d_5-Ethanol and contaminants typical for Tenax GC, were identified as early eluting compounds (contaminants). The potential oxidation products -- acetaldehyde and acetic

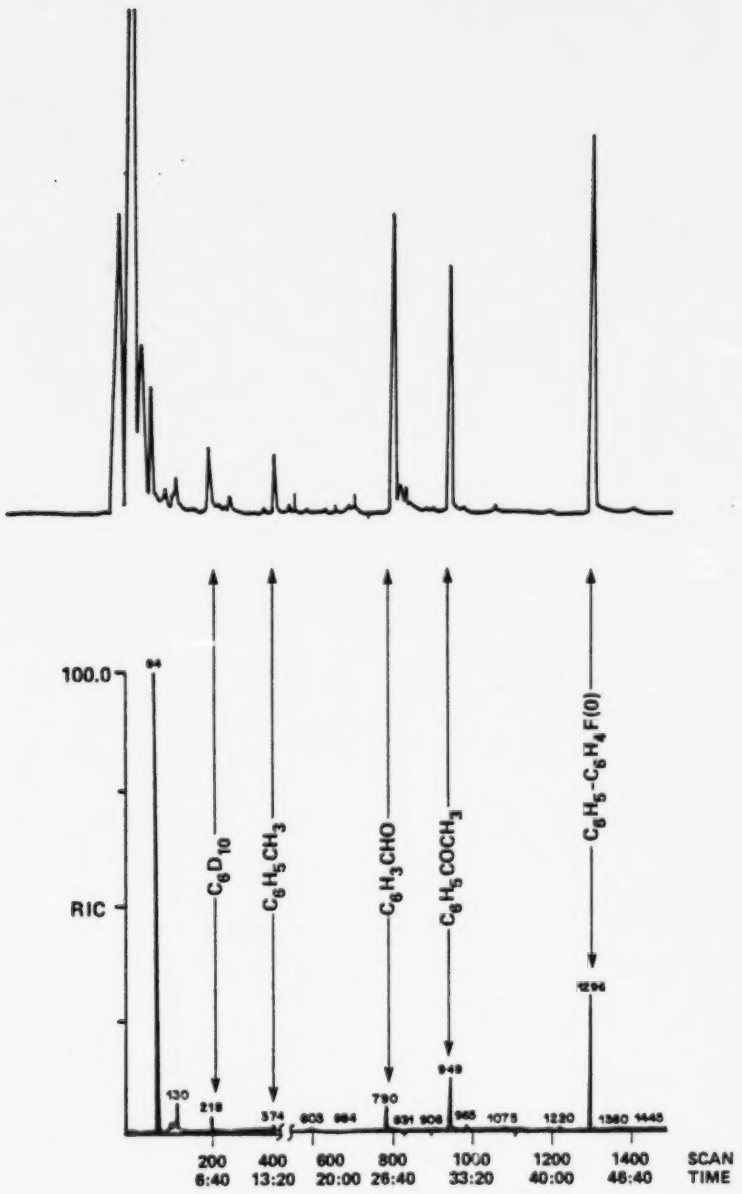


Figure 13. Correspondence of major peaks in GC and GC/MS analysis of duplicate cartridges: A4/A6 - ozone 500 ppb, 50% humidity, d_{10}-cyclohexene, 1.037 ng, internal standard 500 ng.

Table 26. ARTIFACT FORMATION STUDIES USING DEUTERATED COMPOUNDS: CYCLOHEXENE-d_{10}. GC/MS/COMP ANALYSIS (FINNIGAN 3200)

Compound Identified	RRT ± SD[a]	Tenax GC Cartridge					
		C1	A1	A6	B6	A10	B2
Freon II	0.08 ± 0.01	x	x	x			
Acetone	0.10 ± 0.01		x	x			
1,1,2-Trichloro-1,2,2-trifluoroethane	0.10 ± 0.01		x	x			
CH_2Cl_2	0.10 ± 0.03	x		x			
Benzene	0.16	x					
C_6D_{10}	0.16 ± 0.04	x	x	x	x	x	x
C_2HCl_3	0.22 ± 0.03				x	x	x
Toluene	0.26 ± 0.08	x	x	x	x	x	x
Siloxane	0.40			x			
Nonane	0.50 ± 0.08	x			x	x	x
PhCHO	0.61 ± 0.02		x	x	x	x	x
Benzonitrile	0.65 ± 0.02				x	x	x
PhOH	0.65 ± 0.01			x		x	x
$C_8H_{14}O$	0.66						x
Octanal	0.68						x
$PhCOCH_3$	0.73 ± 0.01		x	x	x	x	x
α-Hydroxyacetophenone Benzoic acid methyl ester	0.76 ± 0.01			x	x		
Nonanal	0.76					x	
Decanal	0.87 ± 0.01				x	x	x
2-Fluorobiphenyl	1.00	x	x	x	x	x	x

[a]Relative retention time ± standard deviation.

x = Substance is detected.

Table 27. ARTIFACT FORMATION STUDIES USING DEUTERATED COMPOUNDS: CYCLOHEXANE-d_{10} GC/MS/COMP ANALYSIS (LKB 2091)

Peak No.	Scan No. Samples					m/z (Relative Intensity, %) for 4 most intense peaks	Compound
	B10	B17	A4	B21	C5		
1	270					44(100); 45(100); 46(16); 61(1.8)	
2		290				44(100); 43(8); 41(3); 42(3)	
3	311	330	327	323	311	43(100); 58(52); 42(15); 41(9)	acetone
4		357	353	352	332	49(100); 84(60); 86(43); 51(42)	CH_2Cl_2
5	388	390	420	417	388	43(100); 57(92); 41(68); 56(43)	heptane
6	411		448			83(100); 85(64); 479(30); 48(13)	
7		429				41(100); 42(100); 43(100); 56(100)	
8	479		520	520	482	78(100); 52(20); 51(19); 77(17)	benzene
9	502	555	542	543	504	74(100); 60(83); 42(42); 92(40)	cyclohexene-d_{10}
10		502				97(100); 99(65); 61(51); 63(15)	1,1,1-trichloroethane
11	692		727	729	696	91(100); 92(81); 65(15); 63(11)	toluene
12	757		788	791	762	43(100); 41(60); 56(34); 85(31)	hydrocarbon (C_8H_{18})
13	800	843	828	831		207(100); 208(22); 209(14); 96(12)	
14	893					57(100); 91(93); 43(89); 42(62)	
15				916		91(100); 106(35); 43(25); 57(16)	
16				942		102(100); 76(29); 50(14); 103(12)	
17	960	992	975	979	963	43(100); 57(74); 41(47); 71(27)	hydrocarbon (C_9H_{20})
18		1099	1080		1076	57(100); 56(38); 43(31); 41(23)	hydrocarbon (C_9H_{20})
19	1078	1103	1086	1092	1083	77(100); 106(98); 105(93); 51(55)	benzaldehyde
20				1116		94(100); 66(36); 65(29); 56(16)	
21	1117	1141	1120	1127		103(100); 281(100); 76(32); 282(27)	
23					1121	103(100); 76(34); 50(19); 94(13)	benzonitrile(?)

(continued)

Table 27 (cont'd.)

Peak No.	Scan No. Samples					m/z (Relative Intensity, %) for 4 most intense peaks	Compound
	B10	B17	A4	B21	C5		
24	1140					118(100); 90(40); 89(37); 63(29)	
25		1262	1246			90(100); 88(47); 42(22); 46(21)	dichlorocyclohexane-d_{10}
26	1247	1268	1249	1259	1256	105(100); 77(88); 51(40); 120(38)	acetophenone
27	1254	1274	1257			81(100); 80(60); 77(25); 105(23)	dichlorohexane
28			1290		1294	105(100); 77(65); 51(35); 136(36)	methyl benzoate(?) α-hydroxy-acetophenone (?)
29	1290	1310		1297		57(100); 43(75); 41(75); 44(62)	hydrocarbon
30		1446	1427	1434		41(100); 43(100); 57(76); 55(64)	hydrocarbon
31	1651	1669	1660	1661	1667	172(100); 171(38); 170(28); 173(21)	2-fluorobiphenyl
32				1777		73(100); 281(55); 147(42); 41(39)	

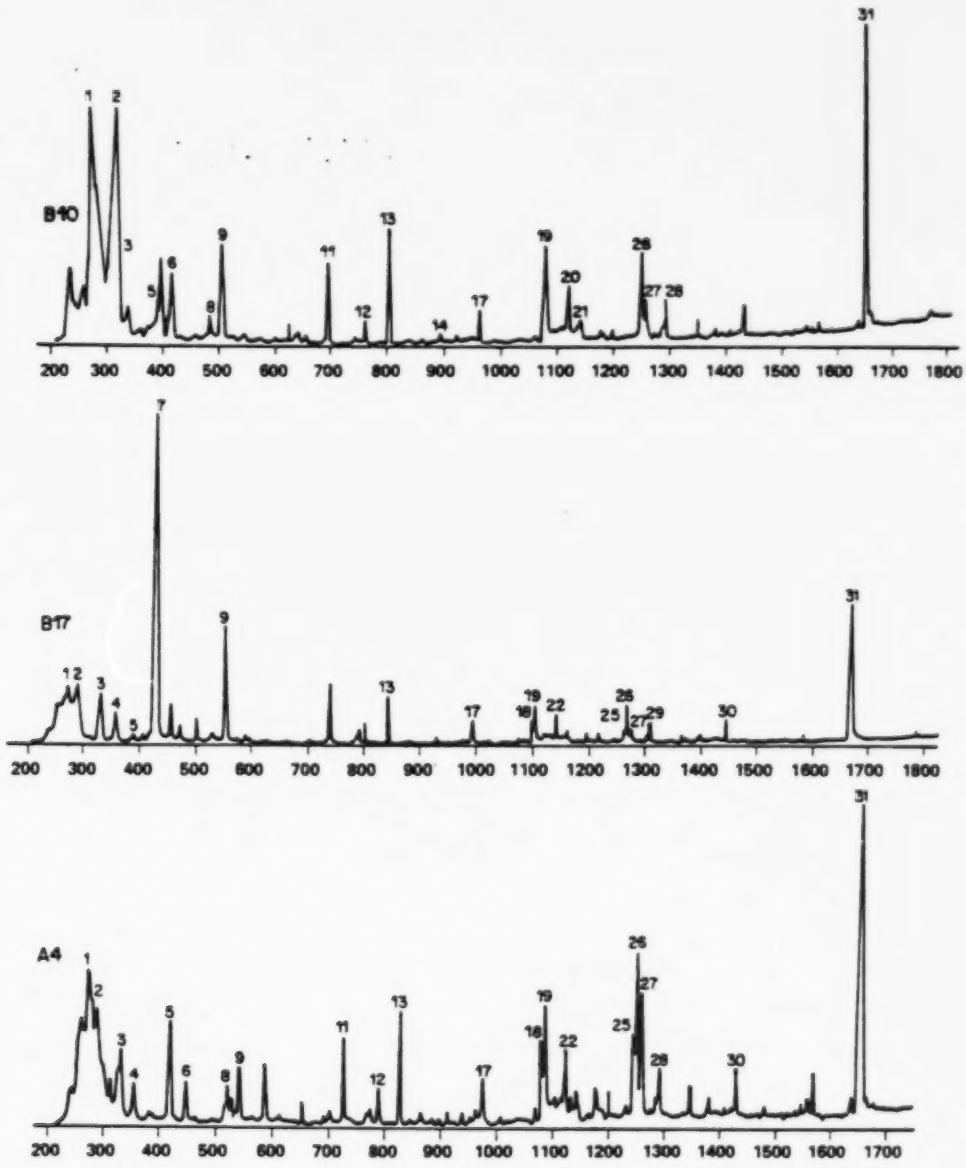


Figure 14. Chlorination of cyclohexene-d_{10}, loaded on Tenax GC cartridges B10, B17, and A4 (peak numbers, as in Table 27) (x-axis: scan number; y-axis: GC response).

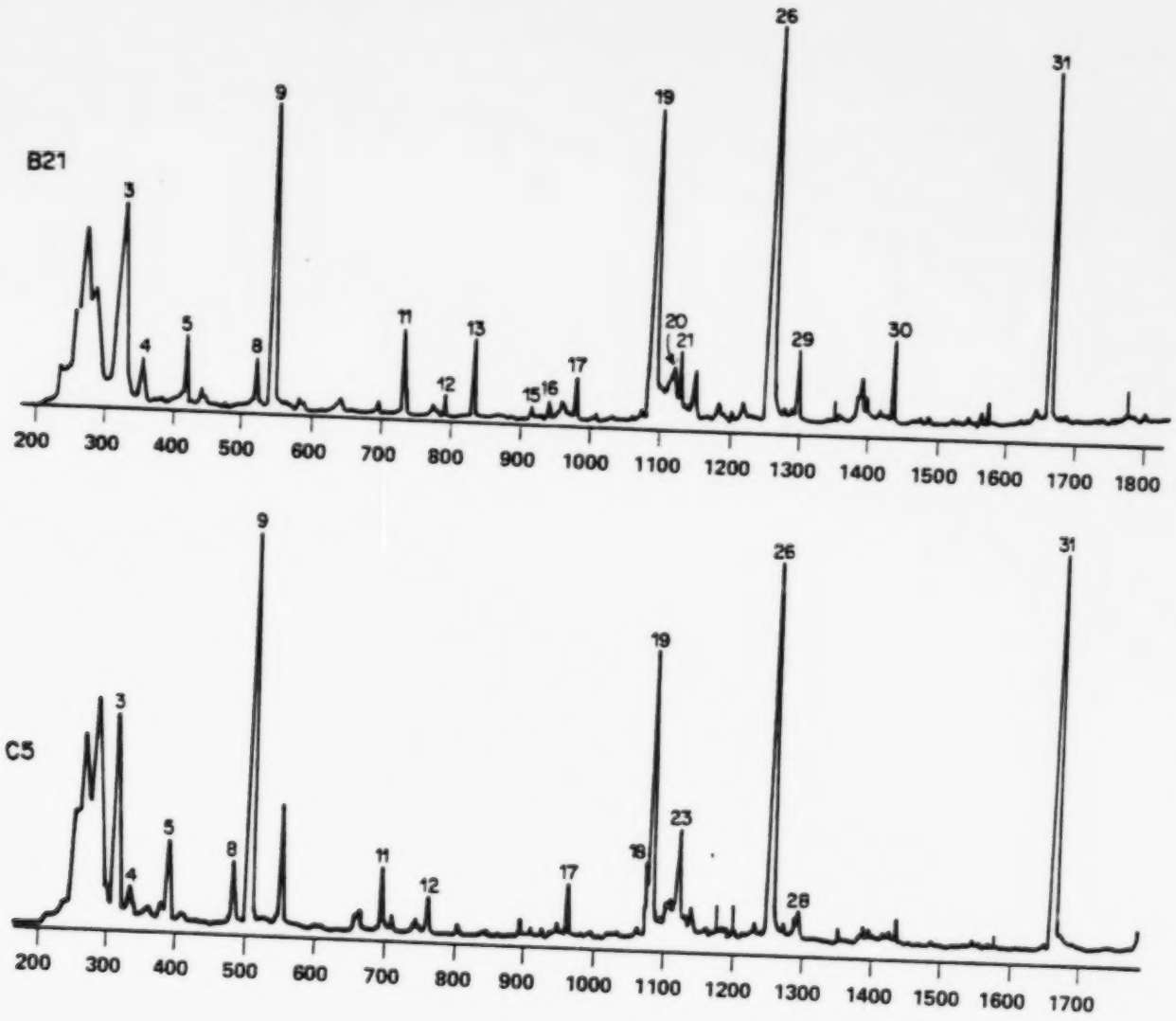


Figure 15. Ozonolysis and ozonolysis/"nitration" of cyclohexene-d_{10} loaded on Tenax GC cartridges B21 and C5 (peak numbers, as in Table 27) (x-axis: scan number; y-axis: GC response).

Figure 16. Thermal desorption - high resolution gas chromatographic analysis of a Tenax GC cartridge loaded with EtOH-d_5 and exposed to a 7.5 L air (500 ppb O_3, 500 ppb NO_x, 50% humidity.

acid -- were not detected in the GC/MS analysis. Deuterated ethanol, and the compounds formed, if any, by reaction with oxidants in sampled air, eluted together with highly volatile contaminants. These compounds were probably outside the limit of Tenax GC sampling capability.

ARTIFACT INHIBITION WITH IMPREGNATED FILTERS

Materials and Methods

The following filters were used for impregnation:

(a) Gelman borosilicate microfiber glass 1.25 mm thick, with acrylic resin binder, 25 mm diameter. Air flow at 34 kPa (5 psi): 12.7 L/min/cm^2. Purified by repetitive 24 h Soxhlet extraction with distilled in glass methanol, and n-pentane, 24 h drying under nitrogen flow, and 48 h drying at 200°C in vacuum oven.

(b) Schleicher and Schuell glass microfiber filters type 25, 0.365 mm, thick, 25 mm diameter (binderless). Air permeability (Gurley): 33 sec.* These filters were used as received.

(c) Schleicher and Schuell polytetrafluoroethylene membrane filters type TE 37, backed with non-woven polypropylene, 24 mm diameter. Maximum pore size 1.0 μm, air permeability (Gurley): 1,000 sec.* These filters were also used as received.

The chemicals used for filter impregnation are listed in Table 28.

The procedure for filter impregnation was as follows:

(a) Five to 10 filters were submerged for 1.5-2 h in 50 mL of a solution of impregnating agents (1 to 10% concentration, see Table 8) in distilled water.

(b) One-half to 1 h drying in air.

(c) Overnight drying in vacuum oven at 50°C.

The filters were weighed before and after impregnation. The filters were tested for the pressure drop, before and after impregnation, using a differential manometer, in an experimental set-up presented in Figure 17. The pressure drop was relatively linear in relation to the flow rate in the

*The average number of seconds required for the displacement of 100 mL of air through an area of 0.65 cm^2 of filter at 1.22 inch of water pressure drop.

Table 28. CHEMICALS USED FOR FILTER IMPREGNATION

Chemical	Formula	Quality	Supplier
sodium thiosulfate	$Na_2S_2O_3$	Anh, 99%	Fisher
sodium metabisulfite	$Na_2S_2O_5$	Cert. ACS, 99.8%	Fisher
sodium oxalate	$Na_2C_2O_4$	Anal. reagent, 99.9%	Mallinckrodt
ammonium sulfamate	$NH_4SO_3NH_2$	Anh, 98%	Sigma
oxalic acid	$(COOH)_2$	98% min	Baker
ferrous sulfate	$FeSO_4 \cdot 7H_2O$	USP, crystal	Fisher
hydrazine hydrate	$N_2H_4 \cdot H_2O$	99% min	Matheson, Coleman, Bell
sodium lauryl sulfate	$C_{12}H_{25}OSO_3Na$	USP	Fisher
sodium hydroxide	NaOH	Cert. ACS, 97% min	Fisher

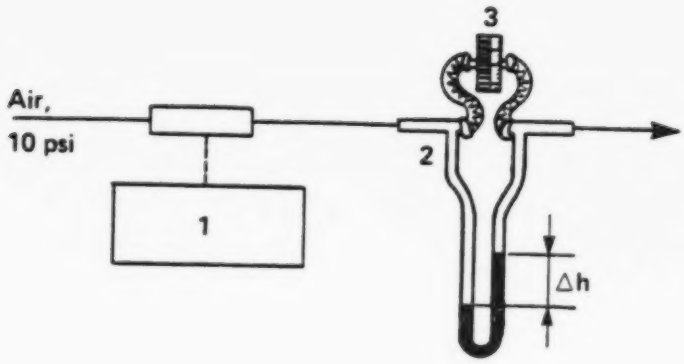


Figure 17. Experimental set-up for pressure drop measurements over the impregnated filters:
(1) "Tylan" mass-flow controller; (2) differential manometer; and (3) "Gelman" filter holder.

range of 0.2 to 1.2 L/min. In Table 28, the pressure drop for a 1 L/min air flow rate is listed. The data are means of at least 3 independent measurements. The "Gelman" filter holders with rubber gaskets were ineffective with S&S filters; Teflon machined cylindrical gaskets were used instead, and the actual filtering area was only 2.84 cm^2. Weight gains and composition of impregnating solutions are also listed in Table 29.

The efficiency of the impregnated filters in quenching ozone and nitric dioxide was tested using the experimental set-up presented in Figure 1. The air flow was 1 L/min and 0.5 L/min (for S&S TE37 filters), with 200 ppb ozone, 400 ppb NO_2 and 50% humidity. After flowing through the filter, the air was directed to the ozone and $NO/NO_2/NO_x$ monitors. The analog output from the monitors was recorded by a strip-chart recorder (Fisher Recordall 4000).

The glass fiber filters GII, GVII, S&S 25-XI, and XII, and the Teflon filters S&S TE37 XIV and XV, were tested for adsorption of organic vapors. This factor was examined by using the system presented in Figure 1, in which the air was passed only through the permeation chamber (100 mL/min) containing a styrene permeation tube (17.5 ng/min permeation rate at 30°C, the lowest permeation rate tube available). Air then flows through a Tenax GC sampling cartridge, with/without the tested filter upstream from the cartridge (Gelman filter holder). The Tenax GC cartridge, after 30 min of sampling, was analyzed by TD-HRGC using the experimental parameters listed in Table 3.

Finally, the Gelman impregnated filters GII and GVII were selected for more in depth testing, involving artifact studies with Tenax GC cartridges and collection efficiencies for styrene vapors.

Tenax GC cartridges were exposed for 30 min to an air flow of 1 L/min containing 200 ppb ozone, 400 ppb NO_x, and 50% humidity, with and without impregnated glass fiber filters upstream from the cartridge. After sampling, the sampling cartridges were loaded with an internal standard, 2-fluorobiphenyl. Using the experimental setup presented in Figure 4, ~2.50 ng of the internal standard (in methanol) was injected through the silicone rubber septum into the glass bulb. The loading process was performed by the "solvent flush technique". The helium flow was 75 mL/min with a loading

time of 10 min. The cartridges were analyzed by thermal desorption-high resolution chromatography under the experimental parameters listed in Table 3.

Results and Discussion

The selection of chemicals for artifact inhibition was guided initially by screening the oxidation potentials. For ozone, the redox potentials are:

$$O_3 + 2H^- + 2e^- \rightarrow O_2 + H_2O \qquad + 2.07\ V$$

$$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^- \qquad + 1.24\ V$$

Because of the high redox potential, several reducing agents are potentially useful as ozone quenching agents. The various agents and filters employed in these experiments are given in Table 29.

The performance of the impregnated filters could not be correlated, however, to a property characteristic of a condensed phase - homogeneous reaction of the impregnating agent. The selection of filters remained an entirely empirical process.

The results of impregnated filters tested for ozone and nitric dioxide quenching are listed in Table 30. A minimum oxidizing agent concentration and the rate (approximately linear) of increase in oxidizing agent concentration downstream from the impregnated filter is given. Two examples of continuous recordings from which the tabulated data were generated are presented in Figures 18 and 19.

The sodium thiosulfate impregnated glass fiber filters (GII and S&S 25-XII) appear to be the best in removing ozone (Table 30). For NO_2 quenching, the results were less spectacular, but relatively good results from GVII were obtained.

The inclusion of sodium lauryl sulfate in the impregnating solution was proposed with the view that a surfactant would lower the surface tension of impregnating solution and allow a better wetting of the filter, and thus an improvement in overall performance. This behavior appeared to be the case for the hydrophobic Teflon filters, which cannot be impregnated uniformly with reducing agents in the absence of surfactants. For the glass fiber filters, reducing agents like oxalic acid, ammonium sulfamate, etc., which were inefficient as quenching oxidants, did not improve with the

Table 29. IMPREGNATED FILTERS FOR OZONE AND NO_2 QUENCHING IN SAMPLED AIR

Filter	Code	Concentration of Chemicals in impreg. sol.,%	Weight, mg ± SD (n)	Weight Gain, %	Pressure Drop mm H_2O at 1 L/min ± SD (n)
G[a]	-	-	104.6 ± 1.6(4)	-	35.8 ± 4.3(3)
G	I	10% $Na_2S_2O_5$	168.3 ± 2.5(2)	60.9	-
G	II	1.5% $Na_2S_2O_3$	110.6 ± 1.2(5)	5.8	35.5 ± 1.3(3)
G	III	2.5% $FeSO_4$[b] 5% NaOH[c]	192.4 ± 2.2(2)	83.9	-
G	IV	10% $(COOH)_2$	181.2 ± 2.4(2)	73.2	-
G	V	10% $2N_2H_4 \cdot (COOH)_2$	156.1 ± 1.7(2)	49.2	-
G	VI	10% $NH_4SO_3NH_2$	183.0 ± 2.1(2)	75.0	-
G	VII	2.5% $FeSO_4$[b] 1% Na_2SO_3[c] 5% N_2H_4 2% NaOH	142.8 ± 1.3(4)	36.5	33.2 ± 11.1(3)
G	VIII	5% $(COOH)_2$ 0.1% NaLS[d]	105.7 ± 0.3(5)	1.1	
G	IX	5% $NH_4SO_3NH_2$ 0.1% NaLS	176.4 ± 3.6(5)	68.7	
G	X	5% $Na_2C_2O_4$	126.2 ± 1.2(5)	20.7	
S&S 25[e]	-	-	34.0 ± 0.7(5)	-	40.3 ± 0.6(3)
S&S 25	XI	5% NaS_2O_3 0.2% NaLS	65.1 ± 2.5(5)	91.5	90.6 ± 6.4(3)

(continued)

Table 29 (cont'd.)

Filter	Code	Concentration of Chemicals in impreg. sol.,%	Weight, mg ± SD (n)	Weight Gain, %	Pressure Drop mm H_2O at 1 L/min ± SD (n)
S&S 25	XII	5% $Na_2S_2O_3$	83.5 ± 2.7(5)	145.5	86.7 ± 7.3(3)
S&S TE(37)[f]	-	-	35.2 ± 2.4(5)	-	217[g]
S&S TE37	XIII	5% $Na_2S_2O_3$ 0.2% NaLS	41.3 ± 0.7(5)	17.3	-
S&S TE37	XIV	10% $Na_2S_2O_3$ 0.1% NaLS	44.6 ± 1.7(5)	26.7	315[g]
S&S TE37	XV	10% $Na_2S_2O_3$ 0.2% NaLS	45.9 ± 1.5(5)	30.4	348[g]

[a]Gelman glass fiber filter.

[b]First solution.

[c]Second solution, filter dried between treatments.

[d]Sodium lauryl sulfate.

[e]Schleicher & Schuell glass fiber filter, type 25.

[f]Schleicher & Schuell Teflon filter, type TE37.

[g]Extrapolated value.

Table 30. QUENCHING OF OXIDANTS IN SAMPLED AIR WITH IMPREGNATED FILTERS

Filter[b]		Ozone Conc. ppb[a]		NO_2 Conc. ppb[a]		Observation
		Minimum	ppb/min[c]	Minimum	ppb/min	
G	I	2.5	7.5	400	0	
	II	0	0	350	0.05	
	III	96	-	320	0.5	
	IV	190	-	400	0	
	V	156	-	400	0	
	VI	-	-	400	0	
	VII	0	0	215	0.5	
	VIII	155	1.3	-	-	
	IX	-	-	400	0	
	X	135	4	-	-	
S&S 25	XI	0	0	-	-	
	XII	0	0	-	-	was 0 ppb O_3 for 14.5 hours
S&S TE 37	XIV	26.5	0.37	-	-	
	XV	26.5	0.25	-	-	
	XV	11	-	-	-	2 filters
	XV	9	-	-	-	3 filters

[a]Mean of two independent measurements.

[b]See Table 29 for filter ID.

[c]Rate of increase in sampled stream after filter.

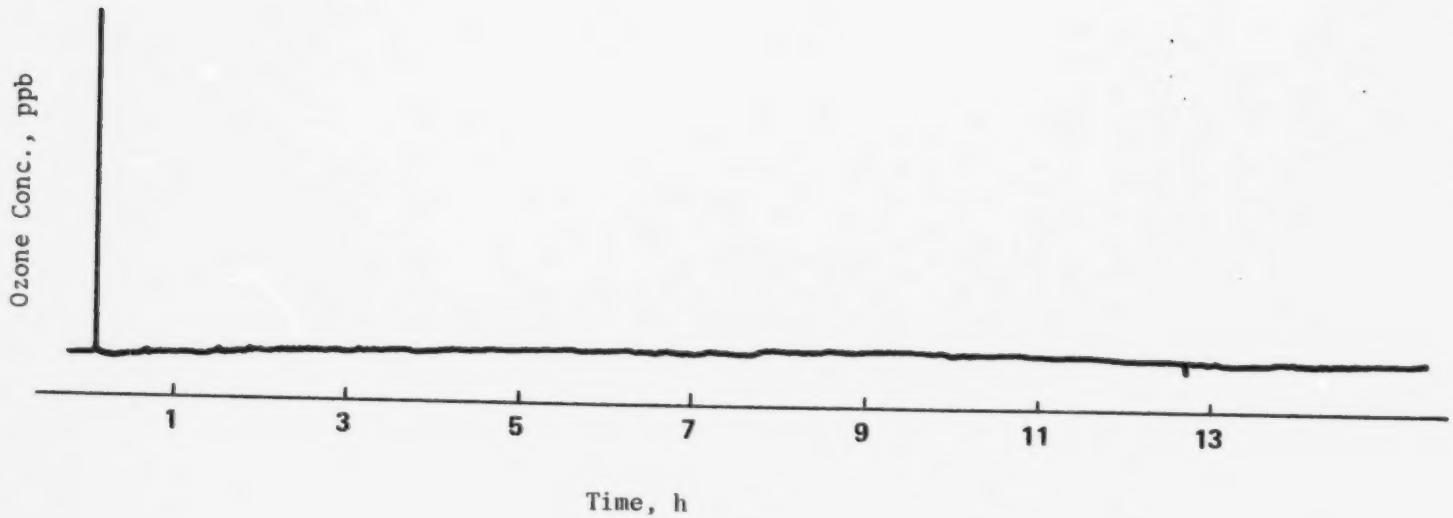


Figure 18. Recorded output of the "Bendix" ozone monitor during test of S&S 25-XII filter for ozone.

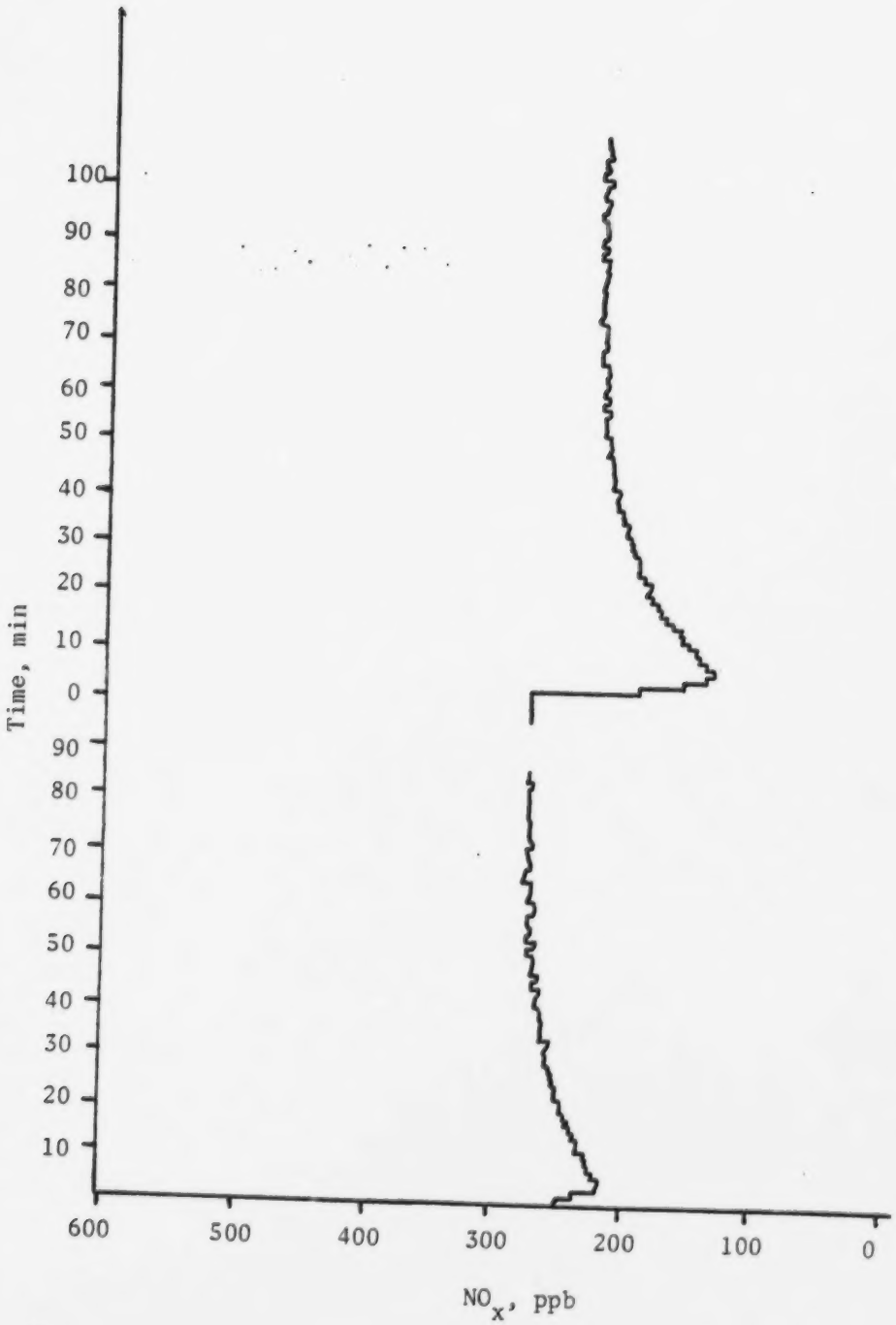


Figure 19. Recorded output of the "Bendix" $NO/NO_2/NO_x$ monitor during test of G-VII filters for nitrogen acids.

addition of surfactant to the impregnating solution. The presence of sodium lauryl sulfate in the sodium thiosulfate impregnating solution had an adverse effect.

The results of using impregnated filters and testing for styrene adsorption are listed in Table 31.

In order to ascertain the statistical significance of the experimental data, the Student t test was performed[11]. The GVII filter reduced significantly the amount of styrene reaching the Tenax GC cartridge. This was not surprising, since the filter was coated with the highly adsorbing $Fe(OH)_2$ gel. For the glass fiber filters impregnated with sodium thiosulfate, it appears that adsorption of styrene vapors does not occur at a significant level. A marginal case was represented by the sodium thiosulfate impregnated Teflon filters. In these cases, there was only a 5 to 10% chance that the observed differences were caused by random error.

The testing results for artifact inhibition on Tenax GC cartridges are listed in Table 32. For a statistical treatment of the data, peak areas of Tenax GC degradation products were normalized relative to the area corresponding to 100 ng of the internal standard:

$$NA = \frac{A_{peak}}{A_{IS}} \times V_{IS}$$

where:

NA = normalized peak area;
A_{peak} = integrated peak area of PhCHO, $PhCOCH_3$ or PhOH;
A_{IS} = integrated peak area for 2-fluorobiphenyl;
V_{IS} = volume of internal standard solution (100 ng/μL) injected.

A statistical analysis of data was performed using the Student t test.[11] The results are tabulated in Table 33.

At the 95% confidence level, the difference between Tenax GC degradation products formed was not statistically significant in any case for phenol, and statistically significant for acetophenone and benzaldehyde (exception, GVII vs. GII). Overall, the artifact formation was significantly reduced, and the protection from filter GVII was slightly better than GII.

In a final test with GII and GVII impregnated filters, styrene was collected from the air stream, and artifact formation was monitored. Thirty liters of air in 30 minutes (200 ppb O_3, 400 ppb NO_x, 50% humidity, styrene

Table 31. TESTING OF IMPREGNATED FILTERS FOR THE ADSORPTION OF STYRENE VAPORS[a]

No.	Filter	Styrene Peak Area x 10^{-3} arbitrary units	x	n	$\bar{s}$[b]	t[c]	1-α[d]
1	none	499	32	7	-	-	-
2	G II	467	31	3	31.7	1.46	<0.90
3	G VII	401	79	3	48.2	2.96	>0.95
4	S&S 25 XI	390	200	2	81.2	1.67	<0.90
5	S&S 25 XII	513	-	1	32	0.40	<0.70
6	S&S TE37 XIV	452	10	2	29.9	1.96	<0.95
7	S&S TE37 XV	452	14	2	30.1	1.95	<0.95

[a]Student t test performed for filter nos. 2 to 7, vs. 1.

[b]Pooled standard deviation:

$$\bar{s} = \left[\frac{(n_1-1)s^2 + (n_2-1)s_2^2}{n_1 + n_2 - 2} \right]^{\frac{1}{2}}$$

[c]
$$t = \frac{\bar{x}_1 - \bar{x}_2}{\bar{s}\,(1/n_1 + 1/n_2)^{\frac{1}{2}}}$$

[d]Comparing with tabulated t values, for $n_1 + n_2 - 2$ degrees of freedom.

Table 32. TESTING THE IMPREGNATED GLASS FIBER FILTERS: ARTIFACT FORMATION ON TENAX GC CARTRIDGES

Cartridge/Filter	GC-ID	Tenax GC Degradation products: Peak Area x 10^{-3}			Internal Standard:Peak Area x 10^{-3} (µl inj.)
		Ph-CHO	$Ph-COCH_3$	PH-OH	
A2/none	312.01	132	46	77	121(2.4)
A3/none	319.01	149	41	106	120(2.5)
A5/GVII	312.02	63	11	42	131(2.5)
A6/GVII	319.03	49	6	19	91(2.5)
A7/GII	312.03	55	18	57	130(2.5)
A8/GII	319.04	87	27	74	171(2.6)

Table 33. TESTING THE IMPREGNATED GLASS FIBER FILTERS BY ARTIFACT FORMATION ON TENAX GC CARTRIDGES: STATISTICAL ANALYSIS OF EXPERIMENTAL DATA

Filter		Normalized Peak Areas for the Tenax GC Degradation Products (Mean ± Standard Deviation)		
		Ph-CHO	$Ph-COCH_3$	Ph-OH
None		2.86 ± 0.34	0.88 ± 0.04	1.87 ± 0.48
GVII		1.28 ± 0.11	0.19 ± 0.04	0.66 ± 0.20
GII		1.19 ± 0.18	0.38 ± 0.04	1.12 ± 0.02
Student t tests (confidence level 95%)				
	Statistically Significant?	Ph-CHO	$Ph-COCH_3$	Ph-OH
Filter GVII versus GII	$\bar{s}$	0.15	0.04	0.14
	t	0.60	4.75	3.29
	1-α	<0.70	<0.99	<0.95
			>0.95	>0.90
	Statistically Significant?	No	Yes	No
Filter GVII versus none	$\bar{s}$	0.25	0.04	0.37
	t	6.32	17.25	2.89
	1-α	>0.95	>0.99	<0.90
		<0.99	<0.999	>0.80
Filter GII versus none	$\bar{s}$	0.27	0.04	0.34
	t	6.19	12.50	2.21
	1-α	>0.95	>0.99	<0.90
		<0.99	<0.995	>0.80
	Statistically Significant?	Yes	Yes	No

428 ppb) were sampled and analyzed. The experimental data are listed in Table 34.

The integrated peak areas were used directly for the statistical analysis, and the results are listed in Table 35.

There was no difference in performance between the two filters, but for both there was a very significant improvement in overall sampling efficiency vs. conventional sampling method. Without filter protection, approximately 85% of the predicted styrene quantity was lost. For the filter GVII, which was known to adsorb some of the styrene from the air stream, the styrene loss was more than compensated for by the protection against degradative action of the oxidants.

For comparison, Figure 20 depicts two chromatographic traces for TD-HRGC analysis of Tenax GC cartridges used to sample styrene in air, with filter GVII and without filter protection (all other experimental parameters were the same).

In conclusion, using impregnated filters upstream from the sampling cartridges significantly improved the collection efficiency and reduced artifact product formation on Tenax GC.

Table 34. TESTING THE IMPREGNATED GLASS FIBER FILTERS: STYRENE COLLECTION EFFICIENCY AND ARTIFACT FORMATION ON TENAX GC

Cartridge/ Filter	GC Run ID	Peaks, Area x 10^{-3} (Retention Time, min)			
		$Ph\text{-}CHCH_2$	PhCHO	$PhCOCH_3$	PhOH
B1/None	312.04	66(10.43)	342(20.17)	91(22.71)	399(24.23)
B2/None	324.03	49(9.30)	285(19.45)	105(22.03)	178(23.63)
Mean Area ± SD		58 ± 12	313 ± 40	98 ± 10	289 ± 156
B3/G II	312.05	358(10.15)	71(20.14)	22(22.70)	52(24.25)
B6/G II	324.04	470(9.27)	151(19.43)	46(22.01)	145(23.61)
Mean ± SD		414 ± 79	111 ± 47	34 ± 17	99 ± 66
B7/G VII	324.05	447(9.32)	116(19.42)	38(22.01)	113(23.61)
B8/G VII	324.06	388(9.16)	59(19.37)	5(21.98)	509(23.58)
Mean ± SD		418 ± 42	88 ± 40	22 ± 23	82 ± 45

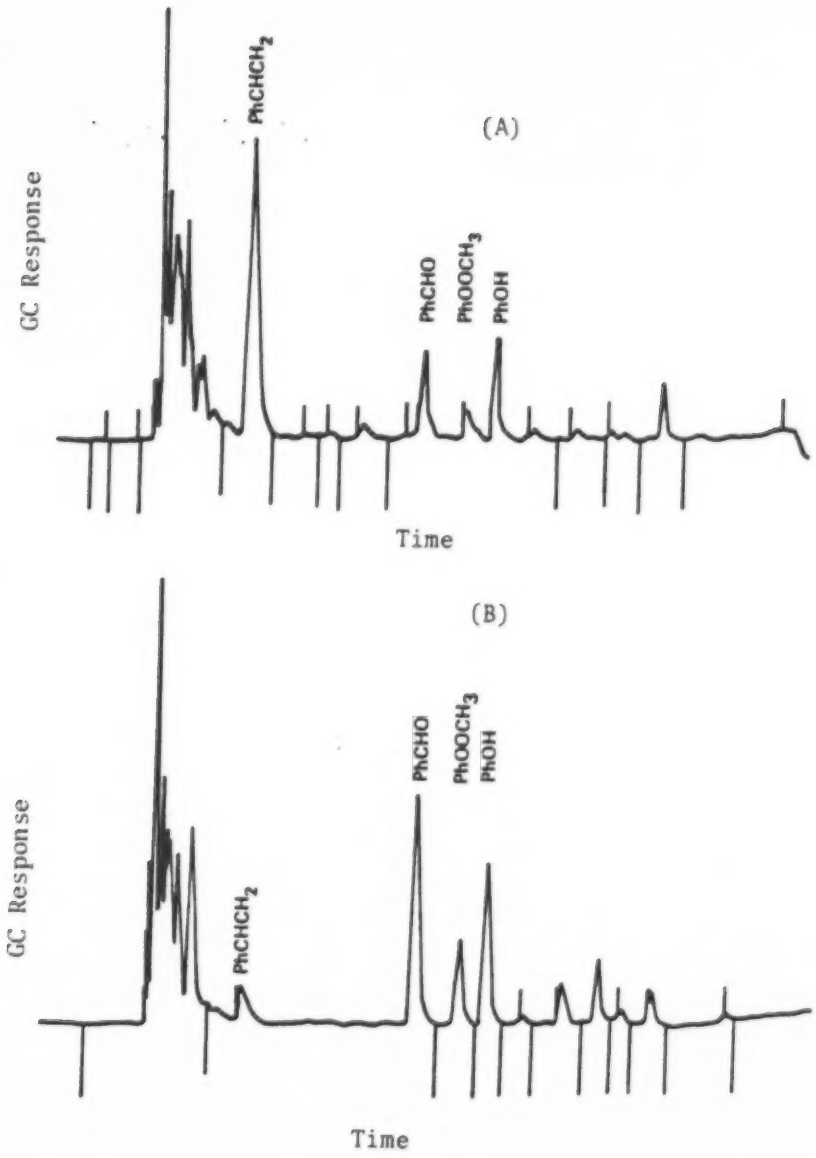


Figure 20. Comparison between sampling for styrene vapors (A) with and (B) without impregnated glass fiber filter protection: "Gelman" G-VII.
Varian 3700, FID, 10^{-11} x 1 x 4 (sens x att).

Table 35. TESTING THE IMPREGNATED GLASS FIBER FILTERS, STYRENE COLLECTION EFFICIENCY AND ARTIFACT FORMATION ON TENAX GC: STATISTICAL ANALYSIS OF EXPERIMENTAL DATA

Student t Test (Confidence Level 95%)	$PhCHCH_2$	PhCHO	$PhCOCH_3$	PhOH
G II versus G VII				
$\bar{s}$	63	49	20	56
t	0.063	0.0469	0.600	0.303
1-α	<0.70	<0.70	<0.70	<0.70
Statistically Significant?	no	no	no	no
G II versus none				
$\bar{s}$	56	49	14	119
t	6.357	4.122	4.571	1.597
1-α	>0.95	>0.90	>0.95	>0.70
	<0.99	<0.95	<0.99	<0.80
Statistically Significant?	yes	no	yes	no
G VII versus none				
$\bar{s}$	31	40	18	115
t	11.612	5.625	4.222	1.800
1-α	>0.99	>0.95	>0.90	>0.70
	<0.999	<0.99	<0.95	<0.80
Statistically Significant?	yes	yes	no	no

SECTION 5

STUDIES ON ARTIFACT PROBLEMS UNDER FIELD SAMPLING CONDITIONS

DESIGN OF A MATRIX FOR FIELD EXPERIMENTS USING DEUTERATED COMPOUNDS

The results from laboratory experiments described in Section 4 suggested two types of filters as the best in overall performance. These were glass fiber filters impregnated with sodium thiosulfate and Teflon filters impregnated with sodium thiosulfate/sodium lauryl sulfate. The major objective in the design of the field experiments was to test of these two types of filters for inhibition of Tenax GC decomposition and for reduction of *in situ* reactions of adsorbed compounds.

Earlier laboratory experiments with deuterated compounds had shown the difficulty in differentiating between sample loss due to reactions with reactive inorganic compounds in air and the sample loss due to stripping by the sampled air, especially for highly volatile compounds. Consequently, deuterated compounds with breakthrough volumes on Tenax GC higher than 40 L (for a 13 mm ID x 60 mm length sorbent bed) at 20°C were chosen for field experiments.

The deuterated compounds selected and the possible artifactual reactions were:

(1) d_{10}-Cyclohexene: chlorination and oxidation;
(2) d_6-Benzene: aromatic substitution and oxidation;
(3) d_8-Dioxane: oxidation (peroxide formation).

In conducting field experiments, two sorbent cartridges were run in parallel. One cartridge was protected by an impregnated filter, the other cartridge by an unimpregnated filter.

The objectives using GC/MS/COMP analysis were to:

(1) assess the recovery of deuterated compounds from exposed cartridges;

(2) identify reaction products of deuterated compounds; and

(3) quantify adsorbed volatile organic compounds, i.e., determine the trends in the quantities found, as related to the use of impregnated filters.

The quantitative technique used included loading cartridges with perfluorinated internal standards (perfluorobenzene and perfluorotoluene) and using relative molar responses.

The field sampling protocol design is presented in Table 36.

FIELD EXPERIMENTS ON ARTIFACT FORMATION

Materials

Tenax GC sampling cartridges (13 mm ID x 60 mm length sorbent bed) were thermally desorbed 4 h at 250°C with helium flow. The background of the desorbed cartridges was checked by thermal desorption-high resolution GC, under the experimental conditions listed in Table 21. Pertinent information on the deuterated compounds used is listed in Table 37.

Approximately 2 μL of the neat deuterated compound was injected (Hamilton 701 G micro-syringe) through a Teflon-lined silicone rubber septum into 1 mL Pierce mini-vials and weighed (Mettler analytical microbalance). Distilled-in-glass redistilled methanol (1 mL) was added to the vial using a calibrated pipet.

The methanolic solutions were used for loading the Tenax GC cartridges by the flash evaporation method. The experimental setup was presented in Figure 4.

For loading a cartridge, 1 μL of the standard solution was injected by the solvent flush technique* into the glass bulb. To minimize adsorption on the walls, the bulb was maintained at ~60°C. The helium flow through the system was 125 mL/min (the loading time was 5 min). Assuming a complete mixing, the ratio between the initial and final concentration of vapors in the helium downstream of the glass bulb was:

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*2-3 μL of the pure solvent (MeOH) were drawn into the syringe barrel, followed by approximately 1 μL air, 1 μL solution, and 2-3 μL air. The exact quantity of the solution injected can be read, and the barrel and syringe needle are flushed with pure solvent during injection.

Table 36. FIELD SAMPLING PROTOCOL

Deuterated Compounds	Filter[a]		No. of Tenax GC Cartridges
	Glass Fiber	Teflon	
d_6-benzene	2/2	2/2	8
d_8-dioxane	2/2	2/2	8
d_{10}-cyclohexene	2/2	2/2	8
none	2/2	2/2	8
controls[b]			5 + 3
	Total No. of Tenax Cartridges		40

[a]Impregnated/not impregnated.

[b]Field controls + laboratory controls.

Table 37. DEUTERATED COMPOUNDS USED TO LOAD TENAX GC CARTRIDGES FOR FIELD EXPERIMENTS

Deuterated Compound	Source	Isotopic Purity	Weight (g), Dissolved in 1 mL MeOH	Ng/Cartridge
d_6-benzene	Stohler Isotope Chemicals, Rutherford, NJ	min 99.5%D	0.001808	1,900
d_8-dioxane	Merck, Sharp & Dohme, Canada, Ltd.	min 99%D	0.004037	4,050
d_{10}-cyclohexene	Merck, Sharp & Dohme, Canada Ltd.	min 98%D	0.001621	1,600

$$C/C_o = \exp(-F \times t/V) = 0.00674$$

where:

F = helium flow rate, 125 mL/min;

t = time, min;

V = glass bulb volume, 125 mL.

The filters used were Gelman borosilicate microfiber, 25 mm, 1.25 mm thick, and a Schleicher and Schuell Teflon filter type TE 37, 25 mm. Filter impregnation (1.5% $Na_2S_2O_3$ aq. for the former, 10% $Na_2S_2O_3$ aq. plus 0.2% aq. sodium lauryl sulphate for the latter), was conducted as described in Section 4.

Field Sampling

Field sampling was performed Friday, October 16, 1981, from 8:45 to 12:05 PM in Elizabeth, NJ, approximately 200 m from Exit 13 on the New Jersey Turnpike, and in the proximity of a petrochemical complex.

The weather condition were sunny and clear with a moderate wind from the southwest, and a temperature of 17 to 25°C.

Sampling was conducted with two cartridges in parallel, each connected to a Nutech Model 221A AC/DC sampling pump.

The sampling train consisted of:

(1) Gelman filter holder;

(2) Filter, one of the following:
Gelman glass fiber, impregnated,
Gelman glass fiber, unimpregnated,
Teflon - TE 37, impregnated,
Teflon - TE 37, unimpregnated,

(3) Tenax GC cartridge (the direction of air flow was the same as the helium flow during the loading of deuterated compounds); and

(4) Drierite trap.

The sampling data are presented in Table 38.

GC/MS/COMP Analysis of Tenax GC Cartridges

For quantitative purposes, the relative molar response (RMR) technique was used[3]. Tenax GC cartridges from the same batch, and prepared exactly in the same way as the cartridges used for field sampling, were loaded with known quantities of the target compounds using a permeation system or a

Table 38. SAMPLING DATA

Cartridge ID	Deuterated Compound[a]	Filter[b]	Volume Air Sampled, liters[c]	Time, From...to	Temp., °C	Observation
F1	Ø	A	19.29	8:45 - 8:53	17	
F2	Ø	B	20.92			
F3	Ø	C	20.35	8:55 - 9:03	17	
F4	Ø	D	21.75			
F6	Ø	A	19.34	9:10 - 9:18	18	
F7	Ø	B	18.25			
F8	Ø	C	19.53	9:22 - 9:30	18	
F9	Ø	D	17.05			
F10	Ø	-	0	0	-	Field blank
F12	-	-	0	0	-	Field blank
F13	Di	-	0	0	-	Field blank
F14	Di	A	21.20	9:32 - 9:40	19	
F15	Di	B	18.28			
F17	Di	A	21.47	9:43 - 9:51	20	
F18	Di	B	20.06			
F19	Di	C	19.79	9:56 - 10:04	22	
F20	Di	D	22.26			
F21	Di	C	18.22	10:13 - 10:21	23	
F22	Di	D	20.03			
F23	Cy	A	20.46	10:36 - 10:44	24	
F24	Cy	B	19.57			
F25	Cy	A	20.96	10:48 - 10:56	24	
F26	Cy	B	20.03			
F28	Cy	C	17.69	11:00 - 11:08	24	
F29	Cy	D	17.91			
F30	Cy	C	25.51	11:12 - 11:22	24	
F31	Cy	D	23.07			

(continued)

Table 38 (cont'd.)

Cartridge ID	Deuterated Compound[a]	Filter[b]	Volume Air Sampled, liters[c]	Time, From...to	Temp., °C	Observation
F32	Cy	-	0	0	-	Field blank
F34	-	-	0	0	-	Field blank
F33	-	A	22.69	11:23 - 11:31	25	
F35	-	B	20.27			
F36	-	A	21.10	11:33 - 11:41	25	
F37	-	B	19.30			
F38	-	C	19.74	11:44 - 11:52	25	
F39	-	D	20.00			
F40	-	C	19.07	11:55 - 12:03	25	
F41	-	D	22.40			
F51	-	-	-	-	-	Laboratory blank
F52	-	-	-	-	-	Laboratory blank
F53	-	-	-	-	-	Laboratory blank

[a] Ø = d_6-Benzene; Di = d_8-dioxane; Cy = d_{10}-cyclohexene.

[b] A = Gelman borosilicate microfiber, impregnated;
B = Gelman borosilicate microfiber, unimpregnated;
C = Teflon TE 37, impregnated;
D = Teflon TE 37, unimpregnated.

[c] Calculated from the Nutech gas meter in cubic feet x 28.3 x pump calibration factor.

"flash evaporation" system. The list of target compounds is presented in Table 39.

All cartridges--exposed, blanks and standards--were loaded just before the GC/MS/COMP analysis with internal standards (perfluorobenzene and perfluorotoluene). Clean nitrogen was spiked dynamically in a permeation system with vapors of the standards (from permeation tubes), and 10 mL of the nitrogen-vapor mixture were injected into the middle of the Tenax GC cartridge with a Precision Sampling gas-tight syringe.

The GC/MS/COMP analysis of Tenax GC cartridges was performed using the experimental parameters listed in Table 40. Selected ion current profiles were used for RMR calculations and for quantitation of target compounds.

Peak areas for one to three most intense ions were used for this calculation:

A_x^y = peak area of compound "y" in the mass-fragmentogram of the ion with $\underline{m}/\underline{z} = x$;

A_u^s = peak area of internal standard "s" in the mass-fragmentogram ion with $\underline{m}/\underline{z} = u$;

The RMR was calculated from the data derived from calibration cartridges, with the relationship:

$$RMR = \frac{A_x^y}{Moles_y} \left[\frac{A_u^s}{Moles_s} \right]^{-1}$$

RMRs for the target compounds are listed in Table 39.

For the quantitation of target substances, A_x^y and A_u^x from the exposed cartridge was used in the relationship:

$$G_y = \frac{A_x^y}{A_u^s} \times \frac{MW^y}{MW^s} \times \frac{G^s}{RMR}$$

where:

G^y = quantity of compound "y", ng/cartridge;
MW^y = molecular weight of compound "y";
MW^s = molecular weight of internal standard "s";
G^s = weight of internal standard "s" in the analyzed cartridge:

$$G^s = 10 \times PR/F \quad (ng)$$

PR = permeation rate of the internal standard, ng/min;
F = nitrogen flow-rate in the permeation system, mL/min.

Table 39. TARGET COMPOUNDS AND RELATIVE MOLAR RESPONSES IN QUANTITATIVE GC/MS/COMP ANALYSIS

Target Compound	Loading Method[a]	Quantity loaded, ng/crt.	Selected ion, m/z	Relative Molar Response	Standard Deviation, n = 6	Coefficient of Variation %
d_6-benzene	B	280	84	0.30	0.051	17
d_8-dioxane	B	438	64	0.045	0.010	23
			96	0.075	0.009	13
d_{10}-cyclohexene	B	378	60	0.087	0.012	14
			74	0.15	0.023	16
			92	0.051	0.008	15
benzene	A	399	78	0.40	0.039	10
toluene	A	199	91	0.71	0.094	13
o-xylene[b]	B	335	91	0.49	0.073	15
			106	0.22	0.043	19
p-xylene	B	335	91	0.49	0.073	15
			106	0.22	0.043	19
ethylbenzene	B	335	91	0.61	0.097	16
			106	0.17	0.036	21
styrene	A	179	104	0.26	0.072	28
isopropylbenzene	B	285	105	0.41	0.121	30
			120	0.10	0.032	31
naphthalene	B	797	128	0.41	0.029	26
chloroform	A	152	83	0.51	0.051	10
			85	0.32	0.034	11
1,2-dichloroethane	A	439	62	0.20	0.031	15
			64	0.069	0.007	11

(continued)

Table 39 (cont'd.)

Target Compound	Loading Method[a]	Quantity loaded, ng/crt.	Selected ion, m/z	Relative Molar Response	Standard Deviation, n = 6	Coefficient of Variation %
1,1,1-trichloroethane	A	242	61	0.19	0.038	20
			97	0.57	0.086	15
			99	0.33	0.037	11
carbon tetrachloride	A	261	117	0.53	0.15	28
			119	0.48	0.12	25
trichloroethylene	A	544	95	0.35	0.039	11
			130	0.35	0.032	9
			132	0.34	0.031	9
1,2-dibromoethane	A	127	107	0.59	0.08	13
			109	0.57	0.059	10
tetrachloroethylene	A	378	164	0.40	0.043	11
			166	0.32	0.055	11
dichlorobenzene	A	243	146	0.72	0.055	8
			148	0.46	0.035	8
acetic acid	B	297	45	0.042	0.032	75
			60	0.040	0.028	70
ethyl acetate	B	285	43	0.20	0.083	41
			88	0.005	0.003	59
benzaldehyde	B	276	77	0.12	0.033	28
			105	0.11	0.037	33
			106	0.11	0.029	26
acetophenone	A	161	77	0.34	0.05	15
			105	0.44	0.097	22
			120	0.11	0.023	21
phenol	A	330	66	0.018	0.008	47
			94	0.065	0.017	26

[a] A = permeation system; B = flash evaporation.

[b] p-Xylene data used.

Table 40. EXPERIMENTAL PARAMETERS FOR THE GC/MS/COMP ANALYSIS OF TENAX GC CARTRIDGES

Instrument:	Finnigan 3300
Column:	60 m fused silica wide bore capillary column, stationary phase DB-1 (J&W)
	Temperature Program: 30° to 240°C/4°C/min
Thermal Desorption:	8 min/250°C injection, from -196°C to 250°C, 1 min 45 sec
Mass Spectrometry:	Scan range: 35 to 350 daltons Sec/scan: 1.9
INCOS Software	

The basic question to be answered was, By using impregnated filter in the sampling process, are the final analytical data changed in a significant way? This question can only be answered by using statistical methods.

If the total variance in the analytical data matrix was caused by only two factors: (a) use of the impregnated/non-impregnated filter in the sampling stage; (b) random errors in the GC/MS/COMP analysis of the cartridge, then a statistical test can be used to assess the significance of the differences between pairs of Tenax GC cartridges (impregnated vs. non-impregnated filters). The hypothesis is, obviously, an oversimplification. Even with pairs of "identical" Tenax GC cartridges (same batch, same treatment, manipulation, etc.), there are other sources of variance in the procedure besides the GC/MS/COMP analysis. The assessment of all sources of variation in the whole analytical technique was a difficult task.

The measure of random errors in the GC/MS/COMP analysis was given by the relative molar response matrix: standard deviations and coefficients of variation for individual RMRs.

Using the F distribution, we can, test the hypothesis that the difference in analytical data between a pair of Tenax cartridges used to sample air under identical conditions (except the nature of the filter), was significantly greater than the expected random error caused by the GC/MS/COMP method. The calculated F value will be compared to the tabulated F for the chosen significance level and the appropriate degrees of freedom[18].

For the quantities of deuterated standards found in a pair of Tenax GC cartridges, the F value will be:

$$F = \left[\frac{x_1 - x_2}{\frac{(x_1 + x_2)}{2} \times \frac{CV}{100}} \right]^2$$

where:

x_1 = ng/cartridge of compound x in cartridge 1;
x_2 = ng/cartridge of compound x in cartridge 2;

while:

$$\frac{\frac{x_1 - x_2}{x_1 + x_2}}{2} \times 100 = \%\text{Difference (Diff) X}$$

and:

$$F = (\%\ \text{Diff/CV})^2$$

The calculated F and % Diff for deuterated compounds are listed in Table 41. If we compare the F's to F for $\alpha = 0.10$ and 1.5 degrees of freedom (F = 4.06), the differences are statistically significant (underlined in Table 41) and positive in only one case (d_{10}-cyclohexene).

It can be inferred that the Gelman impregnated borosilicate filter is providing some protection against sample loss for the relatively more reactive compound, d_{10}-cyclohexene.

The quantitites of benzaldehyde, acetophenone, and phenol--the decomposition products of Tenax GC--also depend on the total volume of air sampled. It was reasonable to expect a proportionality between the two values; the F test should be:

$$c_1 = x_1/V_1$$

$$c_2 = x_2/V_2$$

where:

c_1 = ng/L of compound x for cartridge 1;
c_2 = ng/L of compound x for cartridge 2
V_1 = L air sampled with crt. 1
V_2 = L air sampled with crt. 2

$$\% \text{ Diff} = (c_1 - c_2) \times 100/(c_1 + c_2)$$

$$F = (\% \text{ Diff}/CV)^2$$

The calculated F and % Diff are listed in Table 42, for Gelman $Na_2S_2O_3$ impregnated filter, and Table 43 for Schleicher and Schuell Teflon $Na_2S_2O_3$/ sodium lauryl sulfate impregnated filter.

For the S&S Teflon filter, a positive difference statistically significant only once, and a negative difference was statistically significant eleven times. There was definitely strong evidence that the impregnated filter reduced the artifact formation, i.e., less benzaldehyde, acetophenone, and phenol were formed.

The same conclusion holds for the Gelman borosilicate filter where only negative differences were statistically significant (eight times).

For the target compounds, the data for statistical analysis should be expressed in concentrations, $c_x = x/V$ ng/L of air, basically the same relationship shown above. The calculated F and % Diff are listed in Table 44 for aromatic compounds and Table 45 for halogenated compounds.

Table 41. STATISTICAL ANALYSIS OF DATA: DEUTERATED COMPOUNDS

Compound	Ion, m/z	CV, %	Gelman filter (a) % Diff	Gelman filter (a) F	Gelman filter (b) % Diff	Gelman filter (b) F	S & S filter (c) % Diff	S & S filter (c) F	S & S filter (d) % Diff	S & S filter (d) F
d_6-Benzene	84	17	- 1.00	0.00	+19.00	1.27	+18.46	1.18	-12.28	0.52
d_8-Dioxane	64	23	- 4.46	0.04	+ 4.69	0.04	+ 0.04	0.00	+ 8.88	0.15
	96	13	- 6.61	0.26	+ 4.59	0.12	+ 1.41	0.01	+ 2.09	0.03
d_{10}-Cyclohexene	60	14	+43.15	9.50	- 8.88	0.40	- 1.62	0.01	-11.58	0.68
	74	16	+38.03	5.65	+10.51	0.43	- 1.19	0.01	-13.79	0.74
	92	15	+40.08	7.14	+ 8.64	0.33	+ 1.70	0.01	+ 8.72	0.34

$F(1.5; \alpha = 0.10) = 4.06$. Underlined values indicate significant difference at $\alpha = 0.10$ level.

Table 42. STATISTICAL ANALYSIS OF DATA: ARTIFACT FORMATION, GELMAN FILTER

Compound	Ion, m/z	CV, %	(1) % Diff	(1) F	(2) % Diff	(2) F	(3) % Diff	(3) F	(4) % Diff	(4) F	(5) % Diff	(5) F	(6) % Diff	(6) F	(7) % Diff	(7) F	(8) % Diff	(8) F
Benzaldehyde	77	28	- 0.85	0.00	-26.23	0.88	-10.52	0.01	- 2.75	0.01	-34.03	1.48	-14.84	0.28	- 7.35	0.07	-13.90	0.25
	105	33	+ 1.36	0.00	- 9.42	0.08	-24.67	0.56	+ 4.92	0.02	-40.79	1.53	-19.89	0.36	-16.19	0.24	-18.90	0.33
	106	26	+ 5.69	0.05	- 2.35	0.01	-22.29	0.73	- 0.23	0.00	-39.77	2.34	-21.12	0.66	-12.76	0.24	-11.72	0.20
Acetophenone	77	15	-30.66	4.18	-36.29	5.85	-10.43	0.45	+ 0.65	0.00	-49.76	11.01	-36.66	5.97	- 9.87	0.43	-15.21	1.03
	105	22	-43.62	3.93	-49.22	5.15	-24.19	1.21	-10.97	0.25	-43.17	3.85	-29.74	1.83	-10.19	0.21	- 7.46	0.12
	120	21	-12.17	0.34	+ 0.93	0.00	-27.70	1.68	+44.66	3.77	-66.84	10.13	-36.72	3.06	+11.84	0.32	+ 0.10	0.00
Phenol	66	47	+11.33	0.06	-89.11	3.59	+40.75	0.75	-75.69	2.59								
	94	26	+ 8.88	0.12	-61.45	5.59	-17.91	0.47	-69.97	7.24								

$F(1.5; \alpha = 0.10) = 4.06$. Underlined values indicate significant difference at $\alpha = 0.10$ level.

Table 43. STATISTICAL ANALYSIS OF DATA: ARTIFACT FORMATION, TEFLON FILTER

Compound	Ion, m/z	CV, %	(1)		(2)		(3)		(4)		(5)		(6)		(7)	
			% Diff	F	% Diff	F	% Diff	F	% Diff	F	% Diff	F	% Diff	F	% Diff	F
Benzaldehyde	77	28	- 0.95	0.00	+16.85	0.36	+48.08	2.95	-52.72	3.55	-18.23	0.42	-68.34	5.96	-39.94	2.03
	105	33	+ 6.12	0.03	+ 8.26	0.06	+40.41	1.50	-46.58	1.99	-19.15	0.34	-70.90	4.62	-42.40	1.65
	106	26	+ 3.68	0.02	+ 5.51	0.04	+42.68	2.69	-50.48	3.77	-28.01	1.16	-60.89	5.48	-47.77	3.38
Acetophenone	77	15	+10.77	0.51	+25.35	2.86	+15.37	1.05	-28.03	3.49	-50.05	11.13	-76.37	25.92	-61.98	17.07
	105	22	+14.54	0.44	+82.50	14.06	+39.05	3.15	-24.15	1.20	-34.49	2.46	-61.87	7.88	-59.94	7.42
	120	21	+ 8.23	0.15	+18.70	0.79	- 4.21	0.04	-23.92	1.30	-35.01	2.78	-69.59	10.98	-72.23	11.83
Phenol	66	47	- 6.04	0.02	+87.63	3.43	- 8.66	0.94	-27.51	0.34						
	94	26	-13.50	0.27	+34.84	1.80	+ 6.71	0.07	-62.60	5.80						

$F(1.5; \alpha = 0.10) = 4.06$. Underlined values indicate significant difference at $\alpha = 0.10$ level.

Table 44. STATISTICAL ANALYSIS OF DATA: ARTIFACT REACTIONS OF AROMATIC COMPOUNDS

Compound	Ion, m/z	CV, %	Gelman Filter (a) %Diff	(a) F	(b) %Diff	(b) F	(c) %Diff	(c) F	(d) %Diff	(d) F	Teflon Filter %Diff	Teflon Filter F
benzene	78	10	+11.24	1.26	+8.93	0.80	-5.37	0.29	-2.78	0.08	-2.78	0.08
toluene	91	13	+11.17	0.74	+1.17	0.01	+36.12	7.72	-12.48	0.92	-24.09	3.43
o-xylene	91	15	-0.24	0.00	-1.40	0.58	+7.81	0.27	-3.79	0.06	-11.39	0.58
	106	19	+2.37	0.02	-7.30	0.15	+4.16	0.05	-4.94	0.07	-10.45	0.30
p-xylene	91	15	-2.11	0.02	-11.14	0.55	+7.67	0.26	-10.12	0.46	-10.39	0.48
	106	19	+4.16	0.05	-2.93	0.02	+4.52	0.06	-5.95	0.10	-11.42	0.36
ethylbenzene	91	16	+1.06	0.00	-8.24	0.26	+7.31	0.21	-6.24	0.15	-11.73	0.54
	106	21	+6.88	0.11	+0.20	0.00	+4.99	0.06	-5.56	0.07	-10.91	0.27
styrene	104	28	+11.75	0.18	+1.03	0.00	+15.32	0.30	-22.12	0.62	-12.47	0.20
isopropylbenzene	105	30	+5.54	0.03	-0.67	0.00	+7.49	0.06	-4.59	0.02	+14.49	2.10
	120	31	+12.88	0.17	+7.55	0.06	+11.40	0.14	+2.74	0.01	+26.17	4.05
naphthalene	128	27	-5.50	0.04	-21.53	0.64	+8.91	0.11	-17.08	0.40	+27.01	3.24
											+20.25	1.14
											+22.41	2.23
											+17.18	0.88
											+23.12	2.09
											+17.57	0.70
											+13.53	0.23

(continued)

Table 44 (cont'd.)

Compound	Ion, m/z	CV, %	Gelman Filter (a) %Diff	(a) F	(b) %Diff	(b) F	(c) %Diff	(c) F	(d) %Diff	(d) F
			Teflon Filter (cont'd.)							
			-13.13	0.19	+15.50	0.27				
			-18.30	0.35	+22.06	0.51				
			-13.13	0.24	-	-				

F (1,5). Underlined values indicate significant difference at $\alpha = 0.10$ level.

Table 45. STATISTICAL ANALYSIS OF DATA: ARTIFACT REACTIONS OF HALOGENATED COMPOUNDS

Compound	Ion, m/z	CV, %	Gelman Filter (a) %Diff	(a) F	(b) %Diff	(b) F	(c) %Diff	(c) F	(d) %Diff	(d) F
chloroform	83	10	+19.38	3.76	+20.69	4.28	+144.13	207.62	+49.29	24.29
	85	11	+38.38	12.17	+14.24	1.68	+139.70	161.29	-67.62	37.79
trichloroethane	61	20	-21.95	1.20	-36.18	3.27	+71.81	12.89	-124.68	38.86
	97	15	-17.79	1.41	-20.72	1.91	+58.10	15.00	-121.80	65.94
	99	11	-20.58	3.50	-22.41	4.15	+66.80	31.56	-136.83	154.73
trichloroethyl-ene	95	11	+13.86	1.59	+2.32	0.04	-1.95	0.03	-3.47	0.10
	130	9	+17.46	3.76	+9.12	1.03	-10.43	1.34	+7.36	0.65
	132	9	+23.12	6.60	+7.48	0.69	-12.51	1.93	+4.98	0.31
tetrachloro-ethylene	164	11	+8.20	0.56	+15.05	1.87	+0.97	0.01	-2.08	0.04
	166	11	+6.48	0.35	-0.05	0.00	+4.07	0.14	-5.61	0.26
			Teflon Filters							
			-90.96	82.73	-5.94	0.35				
			-84.52	59.04	-0.06	0.00				
			-40.43	4.09	+31.89	2.54				
			-33.21	4.90	+36.89	6.05				
			-37.46	11.60	+35.75	10.56				
			-7.83	0.45	+23.93	4.73				
			-7.26	0.65	+18.81	4.37				
			-7.84	0.76	+22.72	6.12				
			-6.33	0.33	+22.01	3.65				
			-5.90	0.29	+22.85	4.31				

[a] $F(1,5)$. Underlined values indicate significant difference at $\alpha = 0.10$ level.

The statistical analysis of aromatic compound data (Table 44) was restricted to the higher concentration range, i.e., more than 300 ng benzene/cartridge in order to avoid unaccountable contamination effects. Only once was a positive difference statistically significant (toluene). It can be concluded that the loss of the aromatic compounds by further reaction of adsorbed species was negligible at the level of sensitivity of the analytical method.

The following were excluded from the statistical analysis of the halogenated compound data (Table 45):

(1) 1,2-dichloroethane, because of the high concentration level in air;

(2) 1,2-dibromoethane, practically absent; and

(3) carbon tetrachloride and dichlorobenzene, present at very low concentrations.

Again, the statistical analysis was restricted to the higher concentration range (same Tenax cartridges as for aromatics).

The chloroform and trichloroethane data were erratic and useless in these experiments. For trichloroethylene, a positive difference was statistically significant four times, for tetrachloroethylene only once. Again, there was some evidence that the impregnated filter was preventing a sample loss by further reaction of the adsorbed compound if it was relatively reactive.

It was highly significant that the evidence for sample loss by artifact reaction was positive only for unsaturated compounds (cyclohexene, trichloroethylene, tetrachloroethylene) which were more reactive toward ozone.

The quantities of target compounds in exposed and blank cartridges are listed in Table 46. The standard deviations (and coefficients of variation) of relative molar responses are typical except for acetic acid and ethyl acetate. For these two compounds, accurate quantitation cannot be done by this method. The phenol data are also unreliable. Due to their strong acidic nature, phenol and acetic acid are subject to serious limitations in trace analysis by chromatographic methods; the best deactivated capillaries bind significant quantities irreversibly.

Table 46. RESULTS OF GC/MS/COMP ANALYSIS OF TENAX GC CARTRIDGES

	Compound																										
	d_6-Benzene	d_8-Dioxane	d_{10}-Cyclohexene	Benzene	Toluene	ylene	p-Xylene	Ethylbenzene	Styrene	Isopropylbenzene	Naphthalene	Chloroform	1,2-Dichloroethane	1,1,1-Trichloroethane	Carbon tetrachloride	Trichloroethylene	1,2-Dibromoethane	Tetrachloroethylene	Dichlorobenzene	Acetic Acid	Ethyl acetate	Benzaldehyde	Acetophenone	Phenol
F 14		3334		545	1925	5	1415	418	96	65	426	100	178	300	16	439		883	30	193	405	381	214	342
		3217				457	1268	395		52		98	153	270	16	350		889	28	136	1086	343	214	251
														279		353						331	157	
F 17		3728		425	1175	474	1208	362	60	46	340	11	137	73	7	214		695	21	180		379	251	291
		3451				382	1079	218		33		9	117	71	6	197		681	18	158		371	251	249
														55		198						349	295	
F 15		3486		429	1152	437	1130	335	71	52	336	14	130	122	7	386		754	22	223		365	204	195
		3437				378	1045	324		40		15	129	128	6	335		736	20	22		379	204	259
														127		345						357	178	
F 18		3557		419	1244	460	1249	360	70	45	377	17	156	294	9	207		663	22	1509	154	364	233	603
		3296				375	1070	324		30		17	139	273	11	171		673	19	1151	41	330	233	483
														274		176						327	175	
F 23			1851	119	157	39	110	31			160		64	8		9		135				152	61	37
			1615			33	113	34					50	18		5		144				159	89	63
			1824											6								153	60	
F 25			1130	113	215	49	144	47	7		231		50	16	1	13		170				147	78	51
			1112			42	138	43					46	29	2	10		174				168	114	66
			1268											21								160	96	
F 24			1194	109	190	48	125	39			217		54	3		14		158				205	97	
			1099			37	120	34					50	22		9		158				230	132	
			1215											19								219	115	
F 26			1235	100	186	47	125	39	5		141		54	13				137				163	108	
			1001			40	131	39					35	16				138				196	147	
			1163											16								189	133	
F 33				78	221	51	134	45		4				18		27		176	2			130	72	
						37	130	34		3				30		17		172	1			138	93	
														21								132	92	
F 36				68	205	47	127	42	5					14		20		230	1			156	92	
						42	127	43						20		23		232	1			180	139	
														24								175	116	
F 35				52	185	37	112	25								14		161			125	134	73	
						35	109	32						17		16		159			145	71		
														13		15						92		
F 37				60	190	42	113	37			176	3		17		18		214			164	180	106	
						35	118	36				8		22		17		214			199	98	17	
														22		20						137	63	
F 3	1858			637	1950	677	1786	505	128	105	484	27	196	172	7	458		743	32		367	364	191	
						600	1624	505		88		30	180	180	6	422		740	31		377	226	399	
														171		436						276	349	
F 8	1428			488	1290	456	1211	358	75	51	350	18	165	133	8	317		939	24	755	316	305	181	
						389	1094	345		42		20	149	144	8	290		944	23	859	316	201	431	
														141		306						358	329	

(continued)

Table 46 (cont'd.)

	Compound																								
	d_6-Benzene	d_8-Dioxane	d_{10}-Cyclohexene	Benzene	Toluene	o-Xylene	p-Xylene	Ethylbenzene	Styrene	Isopropylbenzene	Naphthalene	Chloroform	1,2-Dichloroethane	1,1,1-Trichloroethane	Carbon tetrachloride	Trichloroethylene	1,2-Dibromoethane	Tetrachloroethylene	Dichlorobenzene	Acetic Acid	Ethyl acetate	Benzaldehyde	Acetophenone	Phenol
Ion, m/z	84	64 96	60 74 92	78	91	91 106	91 106	91 106	104	105 120	128	83 85	62 64	61 97 99	117 119	95 130 132	107 109	164 166	146 148	45 60	43 88	77 105 106	77 105 120	66 94	
ng/cartridge, in:																									
F 10[a]	2051			168	158	9 4	28 16	7 4			6	16 12	194 173	36 42 36				13 12		661 667		92 95 88	28 33 16		
F 13[a]		4094 3606		84	9	4 1	9 4				6		211 178			5 1 1				92 40		99 90 85	30 27 8		
F 32[a]			1522 1458 1569	45	36	1 1	7 4	2 1			4	10 11	70 76	62 80 65				5 6		29 17		74 85 80	39 40 44		
F 27[a]			1702 1563 1803	35	7						8		64 76	1 10 5						58 54		87 96 76	25 33 34		
F 12[b]				7	13	6 3		11 7	2		6	2 1										101 122	34 38		
F 34[b]				6	2						16											112 85 103	22 4 45		
F 51[c]					1																	94	42		
F 52[c]					3	-																39 35	13 10		
F 53[c]				3	3																	38 43 53	6 6 6		
F 1	1723			777	2053	746 643	1886 1785	561 506	251	115 107	617	28 34	222 211	162 162 156	9 8	232 212 221		1045 1033	41 41	586 573	108 165	45 425 401 408	2 220 219 200	643 520	
F 6	1940			635	1545	520 463	1382 1306	405 412	106	80 72	362	30 33	216 205	197 204 198	6 5	436 411 418	1 1	966 949	27 25	396 382	90 81	315 325 324	163 182 169	213 228	
F 2	1743			753	1991	811 681	2089 1857	602 573	242	115 102	707	25 25	296 271	219 210 208	12 12	219 193 190		1044 1050	28 25			457 429 418	325 370 245	671 518	
F 7	1601			548	1441	550 470	1458 1269	415 388	99	76 63	424	23 27	247 224	268 237 234	5 5	402 354 366		784 896	22 19	754 613		387 337 313	222 286 158	524 406	

(continued)

Table 46 (cont'd.)

	Compound																								
	d_6-Benzene	d_8-Dioxane	d_{10}-Cyclohexene	Benzene	Toluene	o-Xylene	p-Xylene	Ethylbenzene	Styrene	Isopropylbenzene	Naphthalene	Chloroform	1,2-Dichloroethane	1,1,1-Trichloroethane	Carbon tetrachloride	Trichloroethylene	1,2-Dibromoethane	Tetrachloroethylene	Dichlorobenzene	Acetic Acid	Ethyl acetate	Benzaldehyde	Acetophenone	Phenol
F 4	1544			700	2655	811	2118	607	155	128	590	77	231	277	16	527		846	34	376	396	375	188		
						712	1946	602		113		79	219	269	15	485		839	34	304	379	217	459		
														267		504						255	427		
F 9	1616			464	1090	382	1063	312	72	48		21	170	106	8	274		836	20	117	233	252	131		
						349	1006	318		37		22	143	109	6	264		825	19	111	254	136	147		
F 19		3819		301	1058	256	686	192	28	15	281	31	142	108		269						130	202		
		3565				186	586	161		4		32	121	144	4	103		334	7	187	331	288	127		
F 21		3882		168	359	68	194	58			186		177	135	5	74		333	4	97	300	196	203		
		3524				9	132	36					140	121		79						272	193		
F 20		3810		236	389	96	265	77			123	14	151	64		24		93		265	220	202	98		
		3515				71	215	59				11	128	70		11		96		202	223	142	120		
F 22		3552		261	1278	124	325	102	21		277	86	131	6		12						157	99		
		3451				92	256	73				95	108	76		52		128		278	228	210	149		
F 28			1226	103	179	52	145	41			183		68	72		30		134		202	224	189	249		
			1088		.	52	154	41					61	67		31						206	203		
F 30			1303											329		36		157		278	415	372	137		
			1136	95	221	42	119	37			157	19	42	297		27		155		196	394	207	174		
F 29			986			37	117	36				6	36	282		25						220	208		
			1119											18		8		121		19	167	187	95		
			1246	116	229	70	179	57	9		239		70	21		6		127		16	216	77			
F 31			1101			69	188	56					59	20		6						122			
			1281											16		13		165			144	169	105		
			1279	126	271	64	166	54	11	8	257	8	55	29		13		168			169	93			
F 38			1132			55	163	52		5		10	77	24		15						113			
			1221											26		8		148		46	203	251	137		
					67	212	42	134	37		417			29		8		156		21	265	130	108		
F 39						52	130	43						26		11						175	172		
					76	246	55	164	46		660			33		20		186	3	95	288	311	213		
F 41						61	173	60						43		17		196	2	62	348	204	162		
					37	123	21	65	24	3	209	2		39		15						210	187		
						24	69	22				3		6		16		174				133	65		
														14		13		176				163	92		
														6		16						151	63		
														6		18		222				202	125		
														17		17		221				254	173		
														12		20						249	136		
														5		4		62				140	83	14	
														17		5		67				175	108	49	
														10		2						149	86		

[a] Field blanks, loaded with deuterated compounds.

[b] Field blanks, unloaded.

[c] Laboratory blanks.

The quantities of target compounds in laboratory blank cartridges was zero, except for negligible quantities of benzene and toluene, and the ubiquitous Tenax GC decomposition products (benzaldehyde, acetophenone, and phenol).

The field blank cartridges (unloaded) contained moderate contamination by aromatic compounds, the highest value being 16 ng/cartridge of naphthalene. For the loaded field blanks (i,e., deuterated controls), the contamination was considerably higher, but not critical. The contamination could be traced to the solvent (methanol) used to prepare the deuterated compound solutions. 1,2-Dichloroethane was the only case where the quantitation was unreliable because of the high contamination level.

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